Ligand Lability in Carbonyl(η-cyclopentadienyl)triphenylphosphineiron Derivatives

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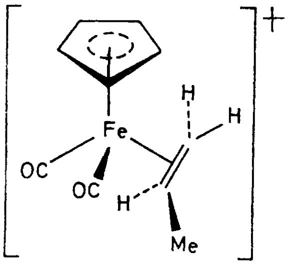
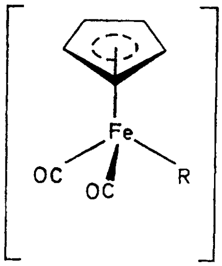
(σ-Allyl)carbonyl(μ-cyclopentadienyl)triphenylphosphineiron undergoes a clean first-order associative process above 40 °C with formation of (1—3-η-allyl)carbonyl(η-cyclopentadienyl)iron and triphenylphosphine, at a rate virtually independent of solvent. Protonation of the former gives a cationic η-propene complex which is very reactive in solution with respect to loss of propene, but more stable in the solid state. Two diastereoisomeric complexes have been observed by n.m.r. spectroscopy in SO$_2$ at −10 °C which gradually release propene to form a further cationic species. Carbonyl(η-cyclopentadienyl)halogeno(triphenylphosphine)iron complexes react under a range of conditions in the presence of Lewis acids to form dicarbonyl(η-cyclopentadienyl)iron derivatives.

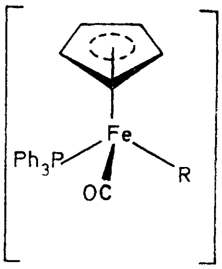
IN the course of an examination of nucleophilic reactions of cationic complexes containing co-ordinated olefins, we reacted dicarbonyl(η-cyclopentadienyl)(η-propene)iron hexafluorophosphate, (I), in diethyl ether suspension with halide-free methyl-lithium and obtained dicarbonyl(η-cyclopentadienyl)methyliron, (IIa), as sole product. Reaction of the corresponding chloride in diethyl ether suspension with phenyl-lithium gave dicarbonyl(η-cyclopentadienyl)phenyliron, (IIb), and (σ-allyl)dicarbonyl(η-cyclopentadienyl)iron, (IIc), in similar amounts, the latter formed by proton abstraction from the allyl methyl group. In neither case was there any evidence of products arising from nucleophilic attack at the co-ordinated olefin. Since there are precedents for expect-



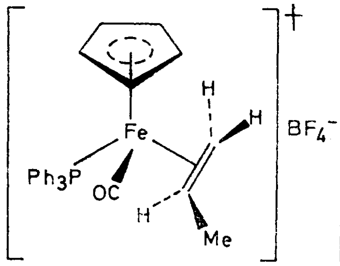
(I)



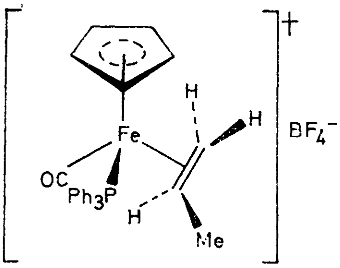
(II) a R=Me
b R=Ph
c R=allyl
d R=Br



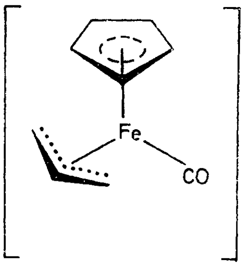
(III) a R=allyl
b R=Br or Cl
c R=CF$_3$CO$_2$
d R=Ph
e R=Pr



(IVa)



(IVb)



(V)

ing this mode of reaction,[1] which was the major point of the investigation, modification of the system was attempted. It was felt that a number of advantages might derive from replacement of one of the carbonyl ligands in complex (I) by triphenylphosphine. There would be considerable steric hindrance to attack at the metal atom, and the superior σ-donor properties of triphenylphosphine might provide a driving force for attack of a nucleophile at olefinic carbon by stabilising an incipient carbon–metal σ-bond. Synthesis of the complex (IIIa), an appropriate precursor to (IV), was accomplished by reaction of (IIIb) with bis(allyl)magnesium, and purification effected by recrystallisation from diethyl ether–isopentane. During preliminary work, vacuum sublimation was attempted, when it was observed that the sublimate contained only triphenylphosphine and (1—3-η-allyl)carbonyl(η-cyclopentadienyl)iron, (V).

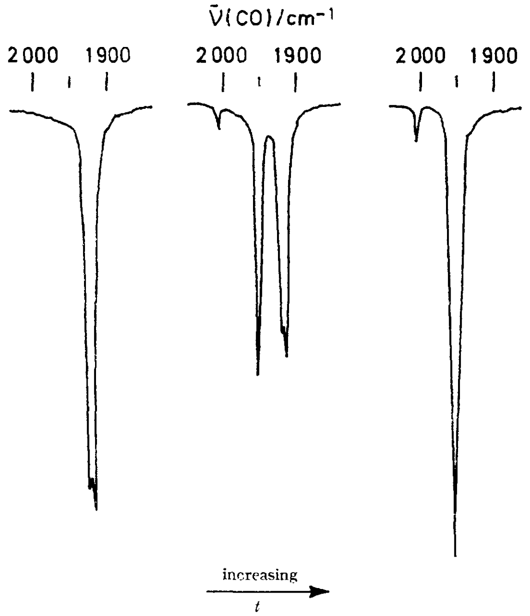


FIGURE 1 Typical i.r. spectra taken during the thermolysis of complex (IIIa) in cyclohexane at 67·5 °C

RESULTS AND DISCUSSION

Thermolysis of Complex (IIIa).—Initial experiments showed that triphenylphosphine loss at 60 °C occurred at a similar rate in cyclohexane, tetrahydrofuran, dimethyl sulphoxide, and acetonitrile, but in the latter two solvents measurement was complicated by the broadness of the carbonyl bands and competing side reactions. In the former two solvents reaction seemed to be much cleaner over several half-lives, the only apparent competing process (Figure 1) being formation of trace amounts of complex (IIc) [ν(CO) at 2 010 cm^{-1}]. No free carbon monoxide was formed, judging by the total absence of new absorbances in the 2 100—2 200 cm^{-1} region.

A series of runs was carried out between 47 and 67 °C, from which it was demonstrated that reaction followed good first-order kinetics over several half-lives, monitoring the decrease in absorbance at 1 918 cm^{-1}. From this data, subjected to computer-based linear least-squares analysis, the first-order rate constants listed in the Table were obtained. In some cases the rate of formation of complex (V) was measured independently and was in good agreement with the rate of decay of (IIIa). It is noteworthy that the phosphine complex thermolysed much more easily, and cleanly, than did (IIc). In the latter case products of homolytic fission including the dicarbonyl dimer (' super sandwich ') were apparent.

Kinetics of thermolysis of (IIIa)

Run	Solvent	θ_0 (±0·2 °C)	$10^5 k_1$/s^{-1}	Activation parameters (at 25 °C)[a]
(1)	C_6H_{12}	67·0	33·7 ± 0·2 (28·4 ± 0·11,[b] 27·0 ± 0·07[c])	
(2)	C_6H_{12}	60·9	15·5 ± 0·08 (13·9 ± 0·08,[b] 14·2 ± 0·010[c])	
(3)	C_6H_{12}	60·9	15·5 ± 0·14	
(4)	C_6H_{12}	47·6	2·57 ± 0·02	$\Delta H^{\ddagger}$ = 26·74 ± 0·22 kcal mol^{-1}
(5)	C_6H_{12}	47·6	2·63 ± 0·02	$\Delta S^{\ddagger}$ = 3·88 ± 0·68 cal K^{-1} mol^{-1}
(6)	C_6H_{12}	47·6	2·38 ± 0·03	
(7)	thf	67·0	26·3 ± 0·2	$\Delta H^{\ddagger}$ = 26·97 ± 1·47 kcal mol^{-1}
(8)	thf	60·6	11·0 ± 0·07 (10·5 ± 0·09,[b] 10·1 ± 0·09[c])	
(9)	thf	47·0	2·305 ± 0·03	$\Delta S^{\ddagger}$ = 2·28 ± 4·42 cal K^{-1} mol^{-1}
(8)	thf	60·6	10·5 ± 0·09	

thf = Tetrahydrofuran.

[a] 1 cal = 4·184 J. [b] Calculated on the decay in absorbance at 1 918 cm^{-1} without assuming a value of A_∞. [c] Calculated on the growth in absorbance at 1 952 cm^{-1}, without assuming a value of A_∞, using program FORWIN.[12]

Displacement of triphenylphosphine and related bases in the course of a σ–η-allyl transformation has previously been reported, and σ–η–σ-allyl interconversions catalysed by phosphines involve a related path.[2] Solvent participation in the rate-determining stage, a process known to be important in some carbonyl displacements, cannot operate here since the reaction rate is very similar in cyclohexane and tetrahydrofuran (Table). Values of $\Delta S^{\ddagger}$ were small, but positive, and, whilst the distinction cannot be definitive, this is more in keeping[3] with an

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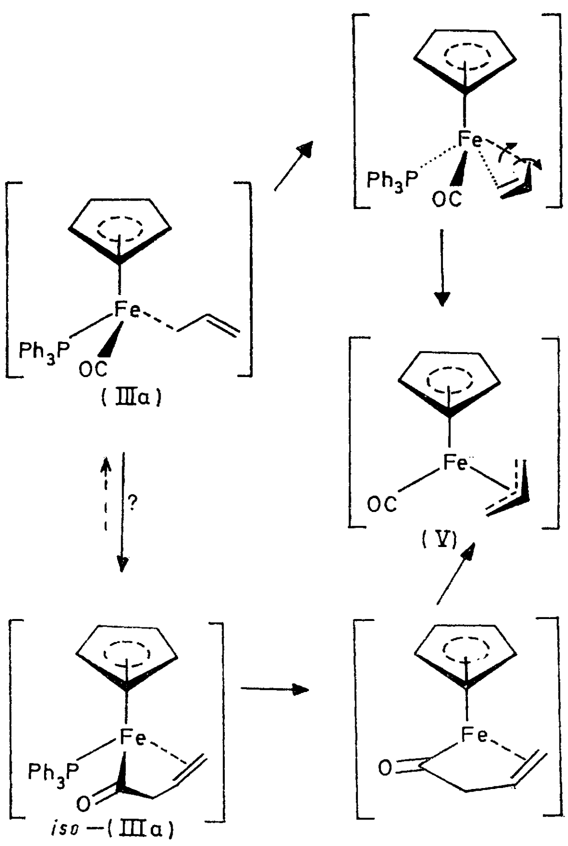
[1] M. L. H. Green and P. L. I. Nagy, *J. Organometallic Chem.*, 1963, **1**, 58; L. Buzetto, A. Palazzi, R. Ros, and U. Belluco, *ibid.*, 1970, **25**, 207; *cf.* D. W. Lichtenberg and A. Wojcicki, *J. Amer. Chem. Soc.*, 1972, **94**, 8271.

[2] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometallic Chem.*, 1966, **6**, 86.

[3] R. J. Angelici, *Organometallic Chem. Rev.*, 1968, **3**, 173; J. P. Candlin and A. C. Shortland, *J. Organometallic Chem.*, 1969, **16**, 289; J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 6927; H. Werner and H. Rascher, *Helv. Chim. Acta*, 1968, **51**, 1765; R. J. Angelici, S. E. Jacobson, and C. M. Ingemanson, *Inorg. Chem.*, 1968, **7**, 2466; C. Cetini, O. Gambino, F. A. Vaglio, and R. P. Ferrari, *ibid.*, 1969, **8**, 1397; R. J. Angelici and G. C. Faber, *ibid.*, 1971, **10**, 514; G. C. Faber and R. J. Angeli, *ibid.*, 1970, **9**, 1586; M. Meier, F. Basolo, and R. G. Pearson, *ibid.*, 1969, **8**, 795; R. D. Johnson, F. Basolo, and R. G. Pearson, *ibid.*, 1971, **10**, 247; R. K. Maples, F. Basolo, and R. G. Pearson, *ibid.*, p. 765; A. J. Hart-Davis and W. A. G. Graham *J. Amer. Chem. Soc.*, 1971, **93**, 4388.

associative (Scheme 1) than with a dissociative path. Given the ease with which *cis*-ligand migration occurs in first-row transition-metal carbonyl alkyls, *iso*- (IIIa) is a possible intermediate, but no pertinent evidence exists at present.

Protonation of Complex IIIa.—Protonation of (IIc) to give salts of complex (I) occurs in a wide range of solvents under moderately acidic conditions.[4] Although the mechanism has not been verified, it is probable that initial protonation is on the iron atom, followed by intramolecular proton transfer. These salts are quite stable in the solid state, and in solution in a variety of polar solvents. Nucleophilic attack by strong nucleophiles has been discussed earlier; with weak nucleophiles such as water slow reaction occurs with displacement of propene and formation of the corresponding cationic aqua-complex.[4]



SCHEME 1

We quickly found that (IIIa) reacted with a range of acids but that the cationic complex so formed was considerably more labile. Addition of hydrogen chloride to a diethyl ether solution produced an immediate pink precipitate, giving red crystals ($\nu_{max.}$ at 1 990 cm^{-1}) on recrystallisation from diethyl ether–sulphur dioxide. Over the course of 1 h these were converted into the chloride (IIIb) ($\nu_{max.}$ at 1 960 cm^{-1}) with expulsion of propene; the same transformation was evident within a few minutes on dissolution in dichloromethane. Addition of trifluoroacetic acid in benzene solution to a solution of complex (IIIa) in the same solvent gave a suspension of a brown oil (presumably the cationic trifluoroacetate) which on shaking for 10 min at room temperature gave a green solution from which [IIIc; $\nu_{max.}$ at 1 961 and 1 699 cm^{-1} (CS_2)] was isolated and characterised. The trifluoroacetate related to (I) is quite stable in solution at room temperature, by contrast. Similar results were obtained in a number of related experiments, from which it was inferred that complex (IV) is unstable with respect to propene loss in chlorinated solvents or in the presence of nucleophilic counter-ions.

A successful preparation of complex (IV) was carried out by employing anhydrous HBF_4 in diethyl ether, and the product was recrystallised from diethyl ether–sulphur dioxide. The resulting product contained diethyl ether, but no sulphur dioxide, and this could not be entirely removed without inducing decomposition. Continued evacuation led to loss of propene and a change in the i.r. stretching wavenumber from 1 992 to 1 979 cm^{-1}. The complex is quite soluble in sulphur dioxide and n.m.r. studies were carried out in this solvent at 220 MHz. If the solution was prepared at −10 °C and stored for a short period at this temperature prior to examination, then several species were observed in solution. Two of these were the diastereoisomers (IVa) and (IVb) or related rotamers, assignments being made by analogy with the corresponding cation (I),[4] assuming that the methyl group in proximity to triphenylphosphine is appreciably more shielded. In addition, small amounts of free propylene and of diethyl ether were discerned. Furthermore, a third cyclopentadienyl resonance (D, Figure 2) was observed at τ 4·50, well downfield from signals of complex (IV) and in equivalent molar amount to free propylene. On standing the solution at 0 °C, signals due to (IVa) and (IVb) decayed in consonance and those due to propene (C) and the third cyclopentadienyl species increased. After 2 h at this temperature only small amounts of complex (IV) remained. It is clear that dissociative loss of propene is taking place, presumably producing complex (VIa) rather than (VII), although it is not entirely certain that SO_2 is co-ordinated, for total evacuation produced an unstable brown-red cation ($\nu_{max.}$ at 1 979 cm^{-1}) with no evidence of co-ordinated SO_2 in the i.r. spectrum. A precedent for an iron-containing sulphur dioxide complex exists in (VIIIa) which also has a pronounced downfield shift of the cyclopentadienyl proton resonance relative to (VIIIb).[5] This implies increased σ-donor contribution from the five-membered ring, rendering it more positively charged; sulphur dioxide would be expected to be a much inferior π-acceptor to propene or ethylene. The greater lability of propene in (IV) than in the corresponding complex (I) may reflect the expected higher stability of the co-

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[4] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1963, 189.

[5] M. L. H. Green and R. L. Whiteley, *J. Chem. Soc.* (*A*), 1971, 1943; *cf.* W. P. Giering and M. Rosenblum, *Chem. Comm.*, 1971, 441.

ordinatively unsaturated cation (VII) when compared to dicarbonyl(η-cyclopentadienyl)iron cation. Alternatively complex (IV) may be destabilised by steric effects involving H–H non-bonded interaction between the aryl rings of triphenylphosphine and propene. Inspection of molecular models suggests that this is feasible.

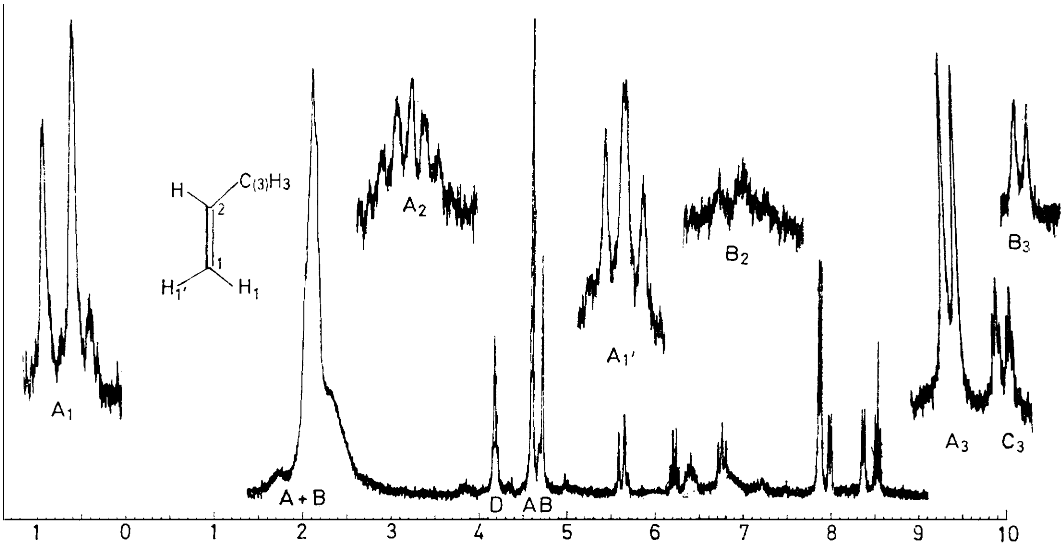
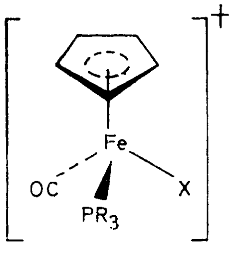
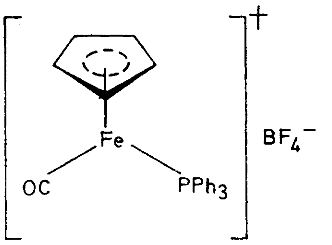


FIGURE 2 220 MHz ^{1}H n.m.r. spectra of complex (IV) in SO_2 at −10 °C after several minutes standing and showing: A and B, major and minor stereoisomers of (IV); C, propene; and D, the propene-free cation (VII) [or (VIa)]. On standing at −10 °C signals due to A and B declined in intensity whilst those due to C and D increased

Disproportionation of Carbonyl(η-cyclopentadienyl)triphenylphosphineiron Derivatives.—Reaction of complex (IIIb) with phenyl bromide–lithium bromide (1 : 1) in diethyl ether proceeded quite differently from the corresponding reaction with phenylmagnesium bromide under otherwise comparable conditions. Whereas the latter gave the corresponding phenyl complex (IIId) in good yield without appreciable side reactions the former gave (IIId) only as the minor product. The major component (60 : 40) was complex (IIb); when the reaction was carried out at −80 °C the ratio was reversed. Our suspicion that formation of the dicarbonyl product involved Lewis-acid-promoted disproportionation of complex (IIIb) followed by attack of phenyl-lithium on (IId) was reinforced by further experiments in which the halide (IIIb) was treated with Lewis acids.

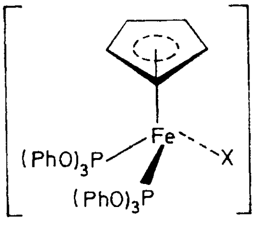


(VI) a R = Ph, X = SO_2
b R = Ph, X = CO
c R = Et, X = CO

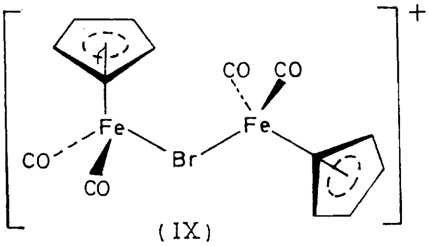


(VII)

In an attempt to determine the mechanism of this unusual transformation, samples of (IIIb) were dissolved in chlorobenzene in the presence of varying amounts of aluminium bromide, and changes in the carbonyl stretching region monitored by i.r. spectroscopy. With 1 mol Lewis acid, an immediate colour change from green to red-brown was observed, but even after several days reaction had only proceeded to the extent of *ca.* 20%.

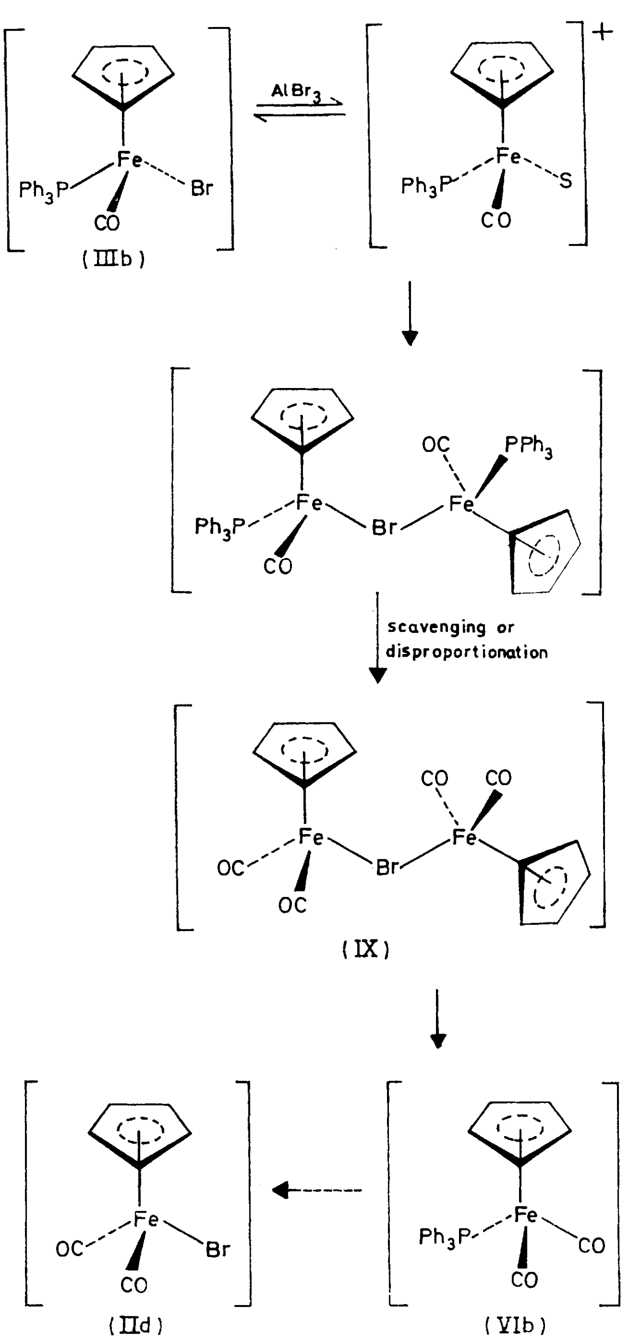


(VIII) a X = SO_2
b X = C_2H_4



(IX)

The only new carbonyl species observed was (IId). With a 50% molar excess of aluminium bromide, a rapid colour change to dark brown was accompanied by a shift in the i.r. stretching wavenumber to 1 979 cm^{-1}, consistent with the formation of complex (VII) (solvated?). This new band decayed at a rather irreproducible rate, and complex (IX) together with (VIb) was observed (proved by comparison with authentic samples). On heating the solution briefly, complex (IId) resulted. In the presence of a four-fold excess of $AlBr_3$ a similar result was obtained, but now the 1 979 cm^{-1} band decayed much more rapidly, albeit with the same result (Figure 3).



SCHEME 2 The counter-ion is $AlBr_4^-$ throughout, S = solvent molecule

Following the work of Haines and du Preez, a tentative mechanism for the process can be suggested (Scheme 2).[6] The nature of the bridged intermediate is unclear but it must have the capacity for rapid carbonyl transfer from one iron atom to the other or rapid and efficient scavenging of carbon monoxide produced in degradative side reactions. Other examples of ligand disproportionation in (η-cyclopentadienyl)iron complexes have been reported, the most pertinent being formation of tricarbonyl(η-cyclopentadienyl)iron cations in chlorination of dicarbonyl(η-cyclopentadienyl)iron dimer.[6] Similarly, Green and Whiteley have shown [5] that (VIIIb) disproportionates on standing in solution with production of the corresponding (η-cyclopentadienyl)tris(triphenyl phosphite)iron cation. The possible intervention of a phosphine-containing bridged dimer is supported by the observation that iodination of complex (X) gave (VIc) as major product (as the iodide) together with some of the neutral dicarbonyl iodide.[7]

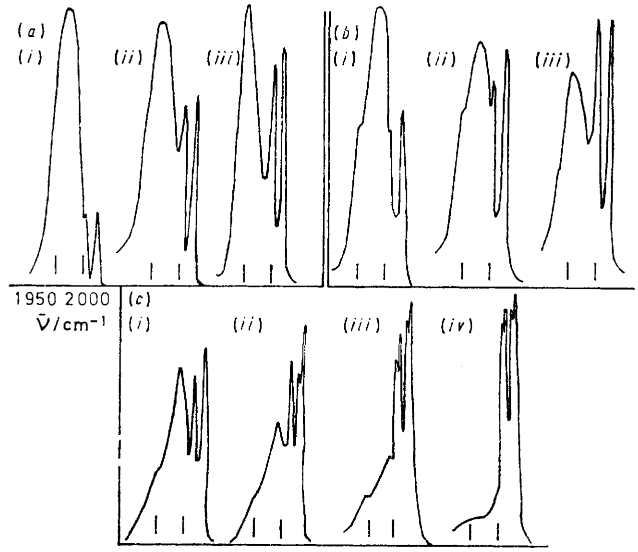
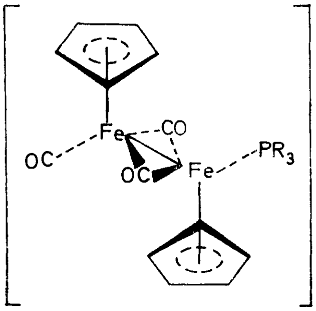


FIGURE 3 I.r. spectra of mixtures of complex (IIIb) and aluminium tribromide in chlorobenzene: (*a*) 1 : 1 molar ratio on mixing (*i*), after 12 h (*ii*), and after 48 h (*iii*). (*b*) 1·5 : 1 molar ratio on mixing (*i*), after 6 h (*ii*), and after 24 h (*iii*); (*c*) 4 : 1 molar ratio on mixing (*i*), after 30 min (*ii*), after 150 min (*iii*), and after 270 min (*iv*)



(X)

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[6] R. J. Haines and A. L. du Preez, *J. Chem. Soc.* (*A*), 1970, 2341; *J.C.S. Dalton*, 1972, 944.

[7] R. J. Haines and A. L. du Preez, *Chem. Comm.*, 1968, 1513.

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 257, 457, and 621 instruments and the carbonyl-stretching region calibrated with polystyrene and/or phenylacetylene. N.m.r. spectra were recorded at 60 (Perkin-Elmer R.12) and 220 MHz (Varian HR-220). M.p.s were determined on a Gallenkamp block and are uncorrected. 'Alumina' refers to Woelm grade 1 material of the appropriate basicity. Combustion analyses were carried out at the Petrochemical and Polymer Laboratories, Runcorn.

Reactions of Dicarbonyl(η-cyclopentadienyl)(η-propene)iron Salts, (I).—(a) Complex (I) (as PF_6^- salt; 0·206 g, 0·57 mmol) was suspended in dry diethyl ether (25 cm^3) and stirred at −78 °C under a dinitrogen atmosphere during addition of an equimolar amount of methyl-lithium in ether (halide-free, from dimethylmercury). After stirring for 30 min at −78 °C a clear yellow supernatant was obtained which was removed by filtration and combined with ether washings of the precipitate. Work-up and sublimation (20 °C, 0·01 mmHg) gave dicarbonyl(η-cyclopentadienyl)-methyliron, (IIa), m.p. 76—77 °C (lit.,[8] 78—82 °C). I.r. spectrum (CCl_4): 2 010vs and 1 923w cm^{-1}. N.m.r. spectrum (C_6D_6): δ 4·1 (s, 5H) and 0·1 p.p.m. (s, 3H). (b) Complex (IIa) (0·182 g, 0·78 mmol) in dry diethyl ether (20 cm^3) was treated with anhydrous hydrogen chloride. Removal of part of the ether together with excess of hydrochloride *in vacuo* gave a yellow suspension which was treated under dinitrogen at −78 °C with an equimolar amount of ethereal phenyl-lithium. The reaction was monitored by i.r. spectroscopy and appeared to be complete after 45 min. Aqueous work-up and chromatography on neutral alumina, eluting with pentane–cyclohexane (1 : 1) gave first (σ-*allyl*)-*dicarbonyl*(η-*cyclopentadienyl*)*iron*, (IIc) (0·068 g, 38%). I.r. spectrum (film): 2 010vs; 1 948vs; 1 608s; 1 190s; and 1 178s cm^{-1}. N.m.r. spectrum (C_6D_6): δ 6·08 (1H, m, H_2); 4·93 [1H, d, H_3(*trans*) $J(H_2-H_3)$ 17 Hz]; 4·68 [1H, d, H_3(*cis*); $J(H_2-H_3')$ 10 Hz]; 4·01 (5H, s, C_5H_5); and 2·10 [2H, d H_1; $J(H_1-H_2)$ 8·5 Hz]. A second fraction (0·089 g, 45%) was characterised after recrystallisation from pentane at −78 °C as dicarbonyl(η-cyclopentadienyl)phenyliron, (IIb), m.p. 33—34 °C (lit.,[9] 34 °C). I.r. spectrum (C_6H_{12}): 2 021vs and 1 979vs cm^{-1}. N.m.r. spectrum (C_6H_{12}): 7·35 (5H, m, Ph) and 4·69 p.p.m. (5H, s, C_5H_5).

Bromocarbonyl(η-cyclopentadienyl)triphenylphosphineiron, (IIIb).—Triphenylphosphine (7·0 g, 0·0343 mol) heated under reflux in pentane (150 cm^3) was treated with bromodicarbonyl(η-cyclopentadienyl)iron (5·0 g, 0·0205 mol) introduced over 24 h by Soxhlet extraction.* A green precipitate was filtered off, washed with n-pentane (3 × 100 cm^3) and diethyl ether (3 × 50 cm^3), and recrystallised from chloroform–light petroleum (b.p. 40—60 °C)to give *bromocarbonyl*(η-*cyclopentadienyl*)*triphenylphosphineiron* (7·66 g, 80%), m.p. 143—144 °C. I.r. spectrum ($CHCl_3$): 1 965 cm^{-1}. N.m.r. spectrum ($CDCl_3$): τ 2·54 (m, 15H, Ph), and 5·52 (s, 5H, C_5H_5).

(σ-*Allyl*)*carbonyl*(η-*cyclopentadienyl*)*triphenylphosphineiron*, (IIIa).—Solid (IIIb) (1·01 g, 2·06 mmol) was added in small portions to a 2M excess of allylmagnesium chloride in diethyl ether (from allyl chloride and magnesium, 0·40M) with efficient stirring under a dinitrogen atmosphere at 0 °C. The resulting red solution was stirred for 30 min and treated with dioxan (5 cm^3 to complex magnesium compounds). The precipitate was filtered off under dinitrogen and the filtrate washed with degassed cold water (2 × 15 cm^3), dried, and solvent removed *in vacuo*. The residue was recrystallised from diethyl ether–i-pentane (1 : 3) giving (σ-*allyl*)-*carbonyl*(η-*cyclopentadienyl*)*triphenylphosphineiron* (0·93 g, 90%), m.p. 104—105 °C (Found: C, 70·65; H, 5·75; P, 7·15. Calc. for $C_{27}H_{25}FeOP$: C, 70·95; H, 5·50; P, 7·05%). I.r. spectrum (CS_2): 3 076w; 3 061m; 3 022vw; 3 004vw; 2 980vw; 2 959w; 2 899w; 2 846w; 1 917vs; 1 200m; 1 184m; 1 118m; 1 090s; 1 029w; 1 022w; 999w; 859w; 819s; 743s; and 698s cm^{-1}. N.m.r. spectrum (C_6D_6) 220 MHz: 6·48 (1H, q, H_2) [$J(H_2-H_3)$(*cis*) 10 Hz, $J(H_2-H_3)$-(*trans*) 17 Hz]; 4·89 [1H, d, H_3 (*trans*)]; 4·74 [1H, d, H_3(*cis*)]; 4·04 (5H, s, C_5H_5); 2·3 (1H, m, H_{1a}); and 1·8 p.p.m. (1H, m, H_{1b}).

Kinetic Investigation of Thermolysis of Complex (IIIa).—Samples of complex (IIIa) in cyclohexane or tetrahydrofuran (*ca.* 5·0 mg cm^{-3}) were prepared in dinitrogen-filled septum-sealed tubes and transferred to a constant-temperature bath. Aliquot portions were removed at intervals by syringe and examined by i.r. spectroscopy, scanning the region 1 800—2 200 cm^{-1} (Perkin-Elmer 621, linear-response mode). Reactions of 67 and 60 °C were taken through at least two half-lives, those at 47 °C through at least one half-life. The data were subjected to linear least-squares analysis to provide the data in the Table.

Protonation of Complex (IIIa) *and Preparation of* (IV).—(a) Complex (IIIa) (0·4617 g, 1·02 mmol) was dissolved in dry diethyl ether (25 cm^{-3}) to give a deep red solution. Exposure to dry hydrogen chloride at room temperature gave an immediate pink precipitate, which was washed with ether and recrystallised from SO_2–Et_2O. The resulting red solid turned green within 1 h, with expulsion of propene (identified by its gas-phase i.r. spectrum). A sample dissolved in dichloromethane changed from red to green within minutes with concomitant loss of absorbance at 1 990 cm^{-1} and appearance of a new absorbance at 1 960 cm^{-1}.

(b) Complex (IIIa) (0·27 g, 0·6 mmol) in benzene (10 cm^3) was treated with an equivalent amount of trifluoroacetic acid in benzene at room temperature. A cherry-red coloured solution was immediately discharged and a brown-red oil adhered to the sides of the vessel. On shaking for 5 min the oil dissolved to give a green solution. Removal of benzene and recrystallisation of the residue from benzene–hexane (3 : 1) gave dark green carbonyl(η-cyclopentadienyl)-triphenylphosphineiron trifluoroacetate [0·14 g, 45%, m.p. 115—117 °C (lit.,[11] 122—123 °C)]. I.r. spectrum (CS_2): 1 961vs; 1 699s; and 1 140s cm^{-1}. N.m.r. spectrum ($CDCl_3$): δ 7·57 (m, 15H) and 4·64 p.p.m. (s, 5H).

(c) Complex (IIIa) (0·98 g, 1·92 mmol) was dissolved in dry diethyl ether (25 cm^3) and ethereal tetrafluoroboric acid (2·1 mmol) was added dropwise. A bright pink-red precipitate formed and was washed with dry diethyl ether (4 × 20 cm^3) and recrystallised from SO_2–Et_2O at −10 °C under dinitrogen. Slow evaporation of SO_2 deposited large red crystals of carbonyl(η-cyclopentadienyl)(η-propene)triphenylphosphineiron tetrafluoroborate, (IV) (0·84 g, 80%) (Found: C, 59·65; H, 4·7; P, 6·20. Calc. for

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* This procedure diminishes the previously reported[10] competitative formation of complex (VIb).

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$C_{27}H_{26}BF_4FeOP$: C, 59·9; H, 4·80; P, 5·90%). I.r. spectrum (chlorobenzene): 1 992 cm^{-1}. N.m.r. spectrum (SO_2): (IVa) δ 7·54 (15H, m, Ph), 5·04 (5H, s, C_5H_5), 4·05 [1H, d, H_1(*trans*); $J(H_1–H_2)$ 14·5 Hz], 3·28 (1H, m, H_2), 2·91 [1H, dd, H_1(*cis*); $J(H_1–H_2)$ 8, $J(H_1–{}^{31}P)$ 8 Hz], 1·80 [3H, d, H_3; $J(H_2–H_3)$ 6·5 Hz]; (IVb) 7·54 (15H, m, Ph), 4·95 [5H, d, C_5H_5; $J(H–{}^{31}P)$ 1 Hz], 2·48 (1H, m, H_2), and 1·28 p.p.m. [3H, d, H_3; $J(H_2–H_3)$ 6 Hz]. Other signals of complex (IVb) were obscured. Traces of diethyl ether, and of complex (VII), were also observed, and the latter increased on standing below 0 °C with concomitant loss of (IV). N.m.r. spectrum of (VII): δ 5·51 p.p.m. (5H, s, C_5H_5). The (IVa) : (IVb) ratio was 7 : 3 throughout.

(d) Dissolution of complex (IV) in chlorobenzene gave a red solution which turned brown within 5 min at room temperature, whilst the i.r. carbonyl stretch changed from 1 992 to 1 979 cm^{-1}. Evolution of propene was demonstrated by running an i.r. spectrum of the gas over the evacuated solution.

Reaction of Bromocarbonyl(η-*cyclopentadienyl*)(*triphenylphosphine*)*iron* (IIIb) *with Phenyl-lithium and Phenylmagnesium Bromide*.—(a) Addition of a 3M excess of ethereal phenyl-lithium to complex (IIIb) (0·75 g, 1·57 mmol) suspended in diethyl ether at −60 °C gave an amber solution, which was washed with oxygen-free water, dried, and ether removed *in vacuo*. Chromatography on neutral alumina with pentane gave first complex (IIb), 0·122 g, m.p. 22—24 °C, 33% [i.r. spectrum (CS_2): 2 020vs; 1 967 vs; 1 941m; 734s; and 699vs cm^{-1}], followed by *carbonyl*(η-*cyclopentadienyl*)*phenyl*(*triphenylphosphine*)*iron*, (IIId) 0·197 g, m.p. 168—169 °C (lit.,[7] 166 °C), 26% [i.r. spectrum (C_6H_{12}): 1 931vs; 1 577w; and 1 119s cm^{-1}].

(b) Addition of a 2M excess of phenylmagnesium bromide to complex (IIIb) (0·71 g, 1·45 mmol) and stirring for 1 h at room temperature gave a deep red solution. Work-up in the usual manner followed by recrystallisation from ether–n-pentane (1 : 4) gave complex (IIId) (0·48 g, 68%).

Disproportionation of Complex (IIId) *with Aluminium Tribromide*.—Samples of complex (IIId) (100 mg) and an appropriate quantity of freshly sublimed aluminium tribromide [run (*a*) molar ratio 1 : 1; (*b*) 1 : 1·5; and (*c*), 1 : 4] were dissolved in chlorobenzene and allowed to stand at room temperature under a dinitrogen atmosphere. Aliquot portions were removed at intervals and changes in the carbonyl-stretching region monitored by i.r. spectroscopy, and direct comparison with authentic samples of complexes (IId), (VIb), and (IX).

We thank the S.R.C. for the award of a studentship under the C.A.P.S. scheme (to K. R. A.), I.C.I. Petrochemical and Polymer Laboratories for facilities, and Dr. P. Moore for the loan of programs FORWIN [12] and ACTPAR and for useful discussions.

[3/1112 *Received*, 30*th May*, 1973]

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