Carbon–Oxygen and –Hydrogen Cleavage in the Reaction of $[Fe_2(CO)_3(\eta\text{-}C_5H_5)_2L]$ [L = $P(OR)_3$ or PR_3] with Phosphite and Phosphine Ligands

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Reaction of $[Fe_2(CO)_3(cp)_2L]$ [cp = η-cyclopentadienyl; L = $P(OMe)_3$ or $P(OEt)_3$] with excess of $P(OR)_3$ yields $[Fe(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ (R = Me or Et), $[Fe(CO)(cp)(COR)\{P(OR)_3\}]$ (R = Me or Et), and $[Fe(CO)(cp)R\{P(OR)_3\}]$ (R = Me) complexes which result initially from phosphite C–O bond cleavage. Reaction of $[Fe_2(CO)_3(cp)_2(PPr_3)]$ with PPr_3 yields $[Fe(cp)_2]$ and $[Fe(CO)(cp)H(PPr_3)]$, the latter arising mainly from hydrogen abstraction from the free phosphine.

IN a previous paper[1] we have shown that $[Ru_2(CO)_4(cp)_2]$ (cp = η-cyclopentadienyl) reacts with trialkyl phosphites in refluxing xylene to yield phosphonate $[Ru(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ and alkyl $[Ru(CO)_2(cp)R]$ complexes resulting from phosphite C–O bond cleavage. Although implicated as the primary product of the reaction, the monosubstituted $[Ru_2(CO)_3(cp)_2\{P(OR)_3\}]$ derivative could not be isolated or detected due to the severity of the conditions needed to initiate reaction of $[Ru_2(CO)_4(cp)_2]$. We have also shown that reaction of the latter compound with tertiary alkylphosphines (PR_3 = PPr_3 or PMe_2Ph) results in hydrogen abstraction from phosphine to yield eventually the hydrides $[Ru(CO)(cp)H(PR_3)]$ and $[Ru(cp)H(PR_3)_2]$ *via* the intermediacy of the monosubstituted $[Ru_2(CO)_3(cp)_2(PR_3)]$ complex which may be isolated. In the case of iron, both monosubstituted phosphite and phosphine derivatives $[Fe_2(CO)_3(cp)_2L]$ [L = $P(OR)_3$ or PR_3] have previously been prepared,[2] and we report here that reaction with excess of ligand yields products analogous to those described above under similar conditions.

RESULTS AND DISCUSSION

The $[Fe_2(CO)_3(cp)_2L]$ complexes [L = $P(OMe)_3$ (1a), $P(OEt)_3$ (1b), and PPr_3 (2)] were prepared as described[2] from $[Fe_2(CO)_4(cp)_2]$ and L in refluxing benzene. Reaction of (1) with a four-fold molar excess of the appropriate phosphite in refluxing xylene proceeded smoothly to yield, after purification, a mixture of the phosphonate $[Fe(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ [R = Me (3a) and Et (3b)] and acyl $[Fe(CO)(cp)(COR)\{P(OR)_3\}]$ [R = Me (4a) and Et (4b)] complexes. In the reaction with $P(OMe)_3$, the alkyl complex $[Fe(CO)(cp)Me\{P(OMe)_3\}]$ (5) was also isolated. Scheme 1 is consistent with that proposed earlier for the reaction of $[Ru_2(CO)_4(cp)_2]$.

The phosphonate complexes (3) have previously been prepared as an inseparable mixture with the $[Fe(CO)_2(cp)\{P(O)(OR)_2\}]$ derivative from reaction of $[Fe(CO)_2(cp)Cl]$ with $P(OR)_3$;[3] $[Fe(CO)(cp)\{P(OMe)_3\}\{P(O)(OMe)_2\}]$ has also been isolated from reaction of $[Fe(CO)_2(cp)(\sigma\text{-}C_5H_5)]$ with $P(OMe)_3$.[4] Both reactions are thought to proceed *via* an Arbusov rearrangement. The CO insertion (iv) has previously been well demonstrated,[5] and we have shown that reaction of $[Fe(CO)_2(cp)Me]$ {prepared from $Na[Fe(CO)_2(cp)]$ and MeI} with $P(OMe)_3$ in refluxing xylene rapidly gives the same mixture of (4a) and (5) observed in the reaction of (1a) with $P(OMe)_3$. While complexes of type (4) are known to undergo slow thermal decarbonylation,[6] analysis of reaction aliquots by n.m.r. spectroscopy during the early stages of the reaction of $[Fe(CO)_2(cp)Me]$ with $P(OMe)_3$ shows that a significant proportion of the complex (5) produced arises probably from a direct carbonyl substitution. A similar observation has been made for the reaction of $[Fe(CO)_2(cp)Me]$ with PPh_3 in ether solvents.[6] No $[Fe(CO)(cp)Et\{P(OEt)_3\}]$ was isolated in the reaction of (1b) with $P(OEt)_3$; it is known, however, that the analogous $[Fe(CO)(cp)Et(PPh_3)]$ is unstable to heat, undergoing elimination of ethylene.[6]

$$[Fe_2(CO)_3(cp)_2\{P(OR)_3\}] \rightleftharpoons [Fe(CO)_2(cp)] + [Fe(CO)(cp)\{P(OR)_3\}] \quad \text{(i)}$$

$$[Fe(CO)_2(cp)] + P(OR)_3 \longrightarrow [Fe(CO)_2(cp)R] + P(O)(OR)_2 \quad \text{(ii)}$$

$$[Fe(CO)(cp)\{P(OR)_3\}] + P(O)(OR)_2 \longrightarrow [Fe(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}] \quad \text{(iii)}$$

$$2[Fe(CO)_2(cp)R] + 2P(OR)_3 \longrightarrow [Fe(CO)(cp)(COR)\{P(OR)_3\}] + [Fe(CO)(cp)R\{P(OR)_3\}] + CO \quad \text{(iv)}$$

SCHEME 1

Reaction of $[Fe_2(CO)_3(cp)_2(PPr_3)]$ (2) with an excess of PPr_3 in refluxing xylene yields ferrocene as the main product. Spectroscopic analysis of the crude reaction product, however, reveals an i.r. absorption at 1 928 cm^{-1}, and a phosphorus-coupled doublet [J(P–H) = 76.2 Hz] at δ −13.9 in the ^1H n.m.r. spectrum † in C_6D_6 assignable to the hydride $[Fe(CO)(cp)H(PPr_3)]$ (6), which could not be isolated but was characterized by conversion into $[Fe(CO)(cp)Cl(PPr_3)]$ (7) on reaction with chloroform.

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† The complex $[Fe(cp)H\{P(OPh)_3\}_2]$ exhibits a triplet resonance at δ −14.05 [J(P–H) = 82 Hz] (A. N. Nesmeyanov, Y. A. Chapovsky, and Y. A. Ustynyuk, *J. Organometallic Chem.*, 1967, **9**, 345).

Analytical and spectroscopic data

	Analysis (%)[a]			N.m.r.[c]	
Complex	C	H	Infrared[b] (cm^{-1})	^{1}H	^{13}C
(3a)[d]	35.3 (34.6)	5.75 (5.25)	1 967	cp 4.76 [t, *J*(P–H) = 0.9] $\mathrm{P(OCH_3)_3}$ 3.68 [d, *J*(P–H) = 12.4] $\mathrm{P(O)(OCH_3)_2}$ 3.53, 3.57 [d, *J*(P–H) = 11.0]	
(3b)[e]	42.9 (42.5)	7.00 (6.60)	1 965	cp 4.69 [t, *J*(P–H) = 0.9] $\mathrm{P(OC}\mathit{H}_2\mathrm{CH_3)_3}$ 4.07 [qnt, *J*(P–H) = 6.7] $\mathrm{P(O)(OC}\mathit{H}_2\mathrm{CH_3)_2}$ 3.89, 3.91 [overlapping qnts, *J*(P–H) = 6.4] $\mathrm{P(OCH_2C}\mathit{H}_3\mathrm{)_3}$ 1.24 [t, *J*(H–H) = 6.9] $\mathrm{P(O)(OCH_2C}\mathit{H}_3\mathrm{)_2}$ 1.17 (overlapping ts)	
(4a)	41.4 (42.3)	5.30 (5.40)	1 939, 1 603	cp 4.61 [d, *J*(P–H) = 1.1] $\mathrm{P(OCH_3)_3}$ 3.58 [d, *J*(P–H) = 11.3] $\mathrm{COCH_3}$ 2.50 [d, *J*(P–H) = 0.5]	cp 83.8 $\left.\begin{array}{l}\mathrm{P(O}\mathit{C}\mathrm{H_3)_3}\\ \mathrm{CO}\mathit{C}\mathrm{H_3}\end{array}\right\}$ 51.5 (coincident) CO 218.0 [d, *J*(P–C) = 46.3] $\mathit{C}\mathrm{OCH_3}$ 61.2 [d, *J*(P–C) = 34.2]
(4b)	48.7 (48.4)	6.75 (6.70)	1 935, 1 602	cp 4.55 [d, *J*(P–H) = 1.0] $\mathrm{P(OC}\mathit{H}_2\mathrm{CH_3)_3}$ 3.92 (qnt) $\mathrm{P(OCH_2CH_3)_3}$ 1.22 [t, *J*(H–H) = 6.9] $\mathrm{COCH_2C}\mathit{H}_3$ 0.82 [t, *J*(H–H) = 7.4] $\mathrm{COC}\mathit{H}_2\mathrm{CH_3}$ 4.00 (q)	cp 83.9 $\mathrm{CO}\mathit{C}\mathrm{H_2CH_3}$ 57.8 [*J*(P–C) = 4.9] $\mathrm{P(O}\mathit{C}\mathrm{H_2CH_3)_3}$ 60.3 [*J*(P–C) = 4.9] $\mathrm{P(OCH_2}\mathit{C}\mathrm{H_3)_3}$ 15.9 [*J*(P–C) = 7.3] $\mathrm{COCH_2}\mathit{C}\mathrm{H_3}$ 10.0 $\mathit{C}\mathrm{OCH_2CH_3}$ 264.5 [*J*(P–C) = 36.6] CO 218.0 [*J*(P–C) = 46.4]
(5)	41.2 (41.7)	6.15 (5.90)	1 943	cp 4.48 [d, *J*(P–H) = 1.1] $\mathrm{P(OCH_3)_3}$ 3.55 [d, *J*(P–H) = 11.3] $\mathrm{CH_3}$ –0.19 [d, *J*(P–H) = 4.9]	cp 82.6 $\mathrm{P(OCH_3)_3}$ 51.3 $\mathrm{CH_3}$ –26.7 [*J*(P–C) = 34.3]
(7)	51.8 (52.3)	7.90 (7.55)	1 955	cp 4.53 [d, *J*(P–H) = 1.2] $\mathrm{P(C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3)_3}$ 1.34—1.93 (m) $\mathrm{P(CH_2CH_2C}\mathit{H}_3\mathrm{)_3}$ 1.00 [t, *J*(H–H) = 7.2]	CO 220.0 [*J*(P–C) = 53.6]

[a] Calculated values are given in parentheses. [b] In hexane solution. [c] In $\mathrm{CDCl_3}$ solution; *J* values in Hz. [d] ^{31}P N.m.r.: $\mathrm{P(OCH_3)_3}$ 180.2, 125.7 [d, *J*(P–P) = 139.2 Hz]. [e] ^{31}P N.m.r.: $\mathrm{P(OCH_2CH_3)_2}$, $\mathrm{P(O)(OCH_2CH_3)_2}$ 179.8, 121.6 [d, *J*(P–P) = 135.4 Hz].

The results are consistent with Scheme 2.

$$[\mathrm{Fe_2(CO)_3(cp)_2(PPr_3)}] \rightleftharpoons [\mathrm{Fe(CO)_2(cp)}] + [\mathrm{Fe(CO)(cp)(PPr_3)}] \qquad \text{(v)}$$

$$[\mathrm{Fe(CO)_2(cp)}] + \mathrm{PPr_3} \longrightarrow [\mathrm{Fe(CO)(cp)(PPr_3)}] + \mathrm{CO} \qquad \text{(vi)}$$

$$[\mathrm{Fe(CO)(cp)(PPr_3)}] + \mathrm{PPr_3} \longrightarrow [\mathrm{Fe(CO)(cp)H(PPr_3)}] \qquad \text{(vii)}$$

SCHEME 2

Thermolysis of (2) under identical conditions in the absence of $\mathrm{PPr_3}$, followed by reaction with $\mathrm{CHCl_3}$ and purification as described, yields ferrocene, $[\mathrm{Fe_2(CO)_4(cp)_2}]$, and $[\mathrm{Fe(CO)(cp)Cl(PPr_3)}]$, the last in an amount much reduced from the reaction of (2) with excess of $\mathrm{PPr_3}$. The presence of $[\mathrm{Fe_2(CO)_4(cp)_2}]$ is indicative of the $[\mathrm{Fe(CO)_2(cp)}]$ radical of equation (v) which in the presence of excess of phosphine would be expected to undergo rapid CO substitution [equation (vi)].* The complex $[\mathrm{Fe_2(CO)_4(cp)_2}]$ is also known to decompose thermally to yield ferrocene.[7] It has recently been reported that $[\mathrm{Fe_2(CO)_3(cp)_2(PPh_3)}]$ decomposes in refluxing benzene to give $[\mathrm{Fe_2(CO)_4(cp)_2}]$ and $[\mathrm{Fe_4(CO)_4(cp)_4}]$.[8] Other properties described indicate a greater lability of $\mathrm{PPh_3}$ as compared to $\mathrm{PPr_3}$, and dissociation of $\mathrm{PPh_3}$ from a 17-electron $[\mathrm{Fe(CO)(cp)(PPh_3)}]$ species may represent a reaction pathway to $[\mathrm{Fe_4(CO)_4(cp)_4}]$.

The reaction scheme outlined is analogous to that postulated for the reaction of $[\mathrm{Ru_2(CO)_3(cp)_2(PPr_3)}]$ with $\mathrm{PPr_3}$, where it has been shown that in the absence of $\mathrm{PPr_3}$ the $[\mathrm{Ru(CO)(cp)H(PPr_3)}]$ formed arises by hydrogen abstraction from the solvent.[1] In the ruthenium case, however, thermal decomposition of the type observed here is not competitive with hydrogen abstraction as no ruthenocene is isolated either in the absence or presence of excess of phosphine.

EXPERIMENTAL

The complexes $[\mathrm{Fe_2(CO)_3(cp)_2L}]$ [L = $\mathrm{PPr_3}$, $\mathrm{P(OMe)_3}$, or $\mathrm{P(OEt)_3}$] [2] and $[\mathrm{Fe(CO)_2(cp)Me}]$ [9] were prepared as described. Solvents were purified and degassed before use. Infrared and n.m.r. spectra were obtained on Perkin-Elmer 257 and JEOL FX-100 instruments respectively; ^{13}C spectra were run in the presence of $[\mathrm{Cr(acac)_3}]$ (acac = acetylacetonate).

Reactions.—$[\mathrm{Fe_2(CO)_3(cp)_2\{P(OEt)_3\}}]$ (1b) *with* $\mathrm{P(OEt)_3}$. Complex (1b) (1.0 g) and $\mathrm{P(OEt)_3}$ (1.0 g) were refluxed in xylene (15 cm^3) until i.r. analysis indicated disappearance of (1b). The solvent was removed and the residue chromatographed on silica gel which had been deactivated by elution with diethyl ether. Benzene eluted $[\mathrm{Fe(CO)(cp)(COEt)\{P(OEt)_3\}}]$ (4b) (400 mg, 26%) as an orange oil, while methanol eluted $[\mathrm{Fe(CO)(cp)\{P(OEt)_3\}\{P(O)(OEt)_2\}}]$ (3b) (500 mg, 27%) as an orange oil. Analytical samples were purified by preparative t.l.c. using 90% diethyl ether–methanol as solvent.

Reaction of $[\mathrm{Fe_2(CO)_3(cp)_2\{P(OMe)_3\}}]$ (1a) with $\mathrm{P(OMe)_3}$ was carried out in the same manner. Elution from the silica gel column with benzene yielded a mixture of $[\mathrm{Fe(CO)(cp)(COMe)\{P(OMe)_3\}}]$ (4a) and $[\mathrm{Fe(CO)(cp)Me\{P(OMe)_3\}}]$ (5) which was separated by preparative t.l.c. to yield (4a) (200 mg, 15%) and (5) (30 mg, 4%) identified spectroscopically by comparison with samples prepared as described below. Elution with methanol yielded [Fe(CO)-

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* Enhanced lability of 17-electron species towards carbonyl substitution has been demonstrated. See, for example, D. R. Kidd and T. L. Brown, *J. Amer. Chem. Soc.*, 1978, **100**, 4095.

(cp){P(OMe)$_3$}{P(O)(OMe)$_2$}] (3a) (300 mg, 18%) as an orange oil which was purified further by preparative t.l.c.

[Fe(CO)$_2$(cp)Me] *and* P(OMe)$_3$. The complex [Fe(CO)$_2$-(cp)Me] (1.0 g) and P(OMe)$_3$ (1.0 g) were refluxed in xylene (25 cm^3) until i.r. analysis indicated disappearance of starting material; n.m.r. analysis at this point showed the presence of (4a) and (5) in the ratio *ca.* 4 : 1. After removal of solvent, the compounds were separated by chromatography on grade IV alumina using CH_2Cl_2 to yield (4a) (1.1 g, 67%) and (5) (250 mg, 17%) as oily orange solids. Analytical samples were obtained by sublimation at 80 °C (0.1 mmHg).*

[Fe$_2$(CO)$_3$(cp)$_2$(PPr$_3$)] (2) *and* PPr$_3$. Complex (2) (0.75 g) and PPr$_3$ (1 g) were refluxed in xylene (15 cm^3) until i.r. analysis indicated disappearance of starting material. Xylene was removed and the residue was dissolved in $CHCl_3$ (15 cm^3) and stirred overnight. After removal of solvent, the residue was chromatographed on grade III alumina using CH_2Cl_2–light petroleum (1 : 1) as eluant. The first orange band yielded ferrocene (200 mg, 35%), while the second green band yielded [Fe(CO)(cp)Cl(PPr$_3$)] (7) (100 mg, 9%) as green crystals [m.p. 79—90 °C (decomp.)] after recrystallization from CH_2Cl_2–light petroleum.

Thermolysis of (2) (0.5 g) in xylene in the absence of PPr$_3$ yielded [Fe$_2$(CO)$_4$(cp)$_2$] (60 mg, 16%), ferrocene (120 mg, 31%), and [Fe(CO)(cp)Cl(PPr$_3$)] (20 mg, 3%).

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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