Carbon Monoxide Reduction. $[Fe(\eta^5-C_5H_5)(Ph_2PCH_2CH_2PPh_2)(CO)H]$: Reactions and Formation by Reduction of the Complex $[Fe(\eta^5-C_5H_5)(Ph_2PCH_2CH_2PPh_2)(CO)]PF_6$ †

Stephen G. Davies,* John Hibberd, Stephen J. Simpson, and Susan E. Thomas
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY
Oliver Watts
Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

The preparation of the cations of $[Fe(\eta^5-C_5H_5)(dppe)(CO)]PF_6$ (1) (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[Fe(\eta^5-C_5H_5)(PPh_3)_2(CO)]PF_6$ (5) and their reduction with $LiAlH_4$ to form the complexes $[Fe(\eta^5-C_5H_5)(dppe)(CO)H]$ (2) and $[Fe(\eta^5-C_5H_5)(PPh_3)(CO)H]$ (6), respectively, is described. Evidence is presented for the intermediacy of $[Fe(\eta^5-C_5H_5)(dppe)(CHO)]$ (4) in the low-temperature reduction of (1). High-temperature reduction of (1) occurs with loss of regioselectivity yielding both $[Fe(\eta^5-C_5H_5)(dppe)(CH_3)]$ (9) and $[Fe(\eta^4-C_5H_6)(dppe)(CO)]$ (8). The latter product is formed exclusively by *exo* attack on the cyclopentadienyl ligand as evidenced by carrying out the reduction with $LiAlD_4$. The disproportionation of (2) in toluene to give $[\{Fe(\eta^5-C_5H_5)(CO)H\}_2(\mu\text{-dppe})]$ (12) and its subsequent thermal and photochemical elimination of dihydrogen has been studied. In contrast, in tetrahydrofuran solutions, (2) disproportionates to (9) *via* (4). The thermal migration of hydrogen from (2) to produce (8) has been studied. The use of $[Fe(\eta^5-C_5H_5)(dppe)(CO)D]$ (3) has shown this migration to be *endo* first-order and intramolecular with a kinetic isotope effect close to unity.

The reductive polymerisation of carbon monoxide (Fischer–Tropsch and related reactions) to hydrocarbons and their oxygenated analogues is becoming increasingly more interesting to industry.[1] Relatively little detail is known, however, about the mechanisms of formation of many of the products.[2] One mechanism for carbon monoxide reduction is believed to proceed sequentially *via* metal–formyl, –hydroxymethyl, and –carbene complexes to produce metal methyl species.

Many examples of kinetically stable metal formyl complexes have been reported recently. Metal formyl complexes have been prepared by hydride reduction of a metal–carbonyl [3-7] or –methoxycarbonyl ligand,[8] by insertion of a metal species into formaldehyde,[8,9] or by formylation of a metal species.[10] An essential feature of the mechanism of the Fischer–Tropsch and related reactions is the conversion of metal carbonyl hydrides to metal methyl *via* prior equilibration of metal carbonyl hydride with metal formyl. The direct insertion of carbon monoxide into a metal hydride to produce a metal formyl has been observed for hydrido(2,3,7,8,12,13,17,18-octaethylporphyrinato)rhodium [11] and in thorium hydride complexes.[12] Metal formyl complexes are thermodynamically unstable species, in general rearranging to carbonyl hydrides or disproportionating to hydroxymethyl complexes. Hydride reduction of metal carbonyl and metal formyl to metal hydroxymethyl has also been observed.[3-9] In general, however, external electrophilic catalysis is necessary to produce metal methyl from metal formyl in these systems.[5,6]

Nucleophilic addition to complexed unsaturated hydrocarbons occurs stereospecifically *exo* onto the unco-ordinated face of the ligand.[13] Cyclopentadienyl is the least susceptible hydrocarbon ligand towards nucleophilic attack.[13,14] Factors which affect the regioselectivity of nucleophilic additions to cationic complexes containing both cyclopentadienyl and carbon monoxide ligands are not well understood. Hydride addition to $[Fe(\eta^5-C_5H_5)(CO)_3]^+$ occurs *exo* onto the cyclopentadienyl ligand,[15] whereas hydride additions to $[Re(\eta^5-C_5H_5)(NO)(L)(CO)]^+$ (L = CO [16] or PPh_3 [3]) cations occur onto the carbon monoxide ligand to generate the corresponding formyl species.

We describe herein the preparation of the carbonyl hydride $[Fe(\eta^5-C_5H_5)(dppe)(CO)H]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), its disproportionation reactions to $[\{Fe(\eta^5-C_5H_5)(CO)H\}_2(dppe)]$ and, *via* the formyl $[Fe(\eta^5-C_5H_5)(dppe)(CHO)]$, to $[Fe(\eta^5-C_5H_5)(dppe)(CH_3)]$, and its rearrangement to $[Fe(\eta^4-C_5H_6)(dppe)(CO)]$. Some of this work has been the subject of preliminary communications.[17]

Results

The cation of $[Fe(\eta^5-C_5H_5)(dppe)(CO)]PF_6$ (1) is most conveniently prepared from $[Fe(\eta^5-C_5H_5)(CO)_2X]$ (X = Br or Cl) in toluene at reflux followed by treatment with trimethylamine *N*-oxide and anion exchange.[18] Reduction of cation (1) with lithium aluminium hydride in dichloromethane–tetrahydrofuran (thf) (1 : 1) or in neat thf at −78 °C produced the iron carbonyl hydride complex $[Fe(\eta^5-C_5H_5)(dppe)(CO)H]$ (2) as the exclusive product with an isolated yield of over 70%. The i.r. spectrum of (2) indicated that the carbonyl ligand was still present (ν_{CO} = 1 910 cm^{-1}). The ^1H n.m.r. spectrum showed that only one of the phosphorus atoms of dppe was co-ordinated to iron since both the cyclopentadienyl (δ 4.15) and the iron hydride (δ −13.23) resonances appeared as doublets due to coupling to a single phosphorus. This structural assignment was confirmed by ^{31}P n.m.r. which was consistent with one bound (δ 84.8) and one free (δ −13.5) phosphorus atom. No P–P coupling constant could be resolved for (2). The mass spectrum of (2) did not show a molecular ion; however $M - 1$ at m/z 547 was present.

Reduction of cation (1) with lithium aluminium deuteride in thf resulted in the formation of the carbonyl deuteride (3) analogous to the carbonyl hydride (2). No iron hydride could be detected in the ^1H n.m.r. spectrum of (3) and the ^2H n.m.r. spectrum showed that all the deuterium present in (3) was bound to iron.

Lithium aluminium hydride or $LiBEt_3H$ was added to solutions of cation (1) in $[^2H_8]$thf at −78 °C. These solutions were monitored by ^1H n.m.r. spectroscopy as the temperature was slowly raised. Between −70 and −50 °C both solutions developed a resonance at δ 11.53 characteristic of a metal formyl proton.[4] Table 1 shows the chemical shifts of known

---

† *Non-S.I. unit employed:* cal = 4.184 J.

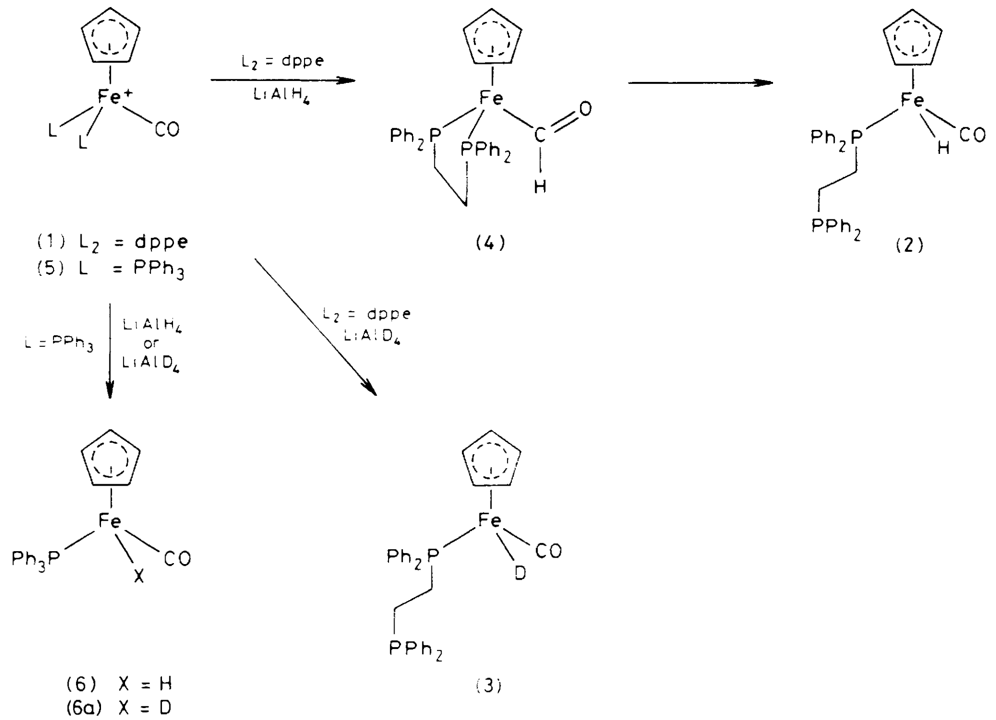


Table 1. ^{1}H N.m.r. chemical shift of iron formyl species

	δ/p.p.m.	Ref.
$[Fe(CO)_4(CHO)]^-$	14.95	*a*
$[Fe(CO)_3\{P(OPh)_3\}(CHO)]^-$	14.82	*a*
$[Fe(\eta^5-C_5H_5)(CO)(COC_6H_4OMe-p)(CHO)]^-$	13.10	*b*
$[Fe(\eta^5-C_5H_5)(CO)(COC_6H_5)(CHO)]^-$	12.91	*b*
$[Fe(\eta^5-C_5H_5)(CO)(COMe)(CHO)]^-$	12.83	*b*
$[Fe(\eta^5-C_5H_5)(dppe)(CHO)]$	11.53	This work

[a] C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, 1976, **98**, 5395. [b] J. C. Selover, M. Marsi, D. W. Parker, and J. A. Gladysz, *J. Organomet. Chem.*, 1981, **206**, 317.

iron formyl species for comparison. Above −50 °C the formyl rapidly disappeared. Work-up led to the isolation of (2) as the sole product strongly supporting the hypothesis of the formyl species $[Fe(\eta^5-C_5H_5)(dppe)(CHO)]$ (4) being an intermediate in these reductions.

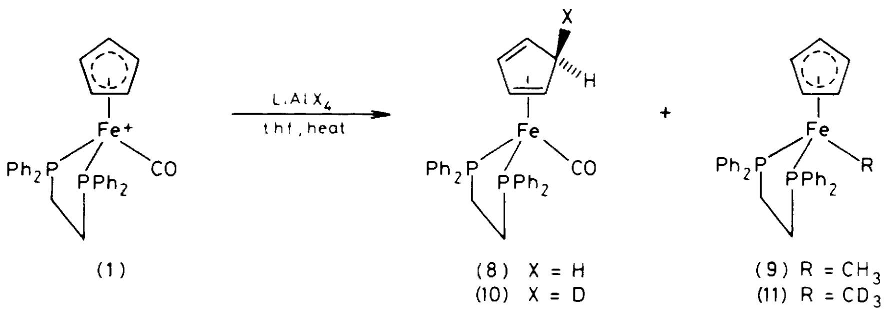
Similarly, $LiAlH_4$ reduction of $[Fe(\eta^5-C_5H_5)(PPh_3)_2(CO)]PF_6$ (5) at −78 °C in thf–dichloromethane yielded the carbonyl hydride $[Fe(\eta^5-C_5H_5)(PPh_3)(CO)H]$ (6) as the sole product. Reduction of (5) with $LiAlD_4$ gave the corresponding iron deuteride complex (6a).

A ^{31}P n.m.r. saturation transfer experiment in which one of the phosphorus atoms of the carbonyl hydride (2) was saturated and completely inverted by means of a DANTE sequence[19] clearly demonstrated that the co-ordinated and unco-ordinated phosphorus atoms were rapidly exchanging with an upper limit for $\Delta G^\ddagger$ of 18 kcal mol^{-1}. No exchange of phosphorus atoms could be detected in $[Fe(\eta^5-C_5H_5)\{PPh(CH_2CH_2PPh_2)_2\}H]$ (7).[20]

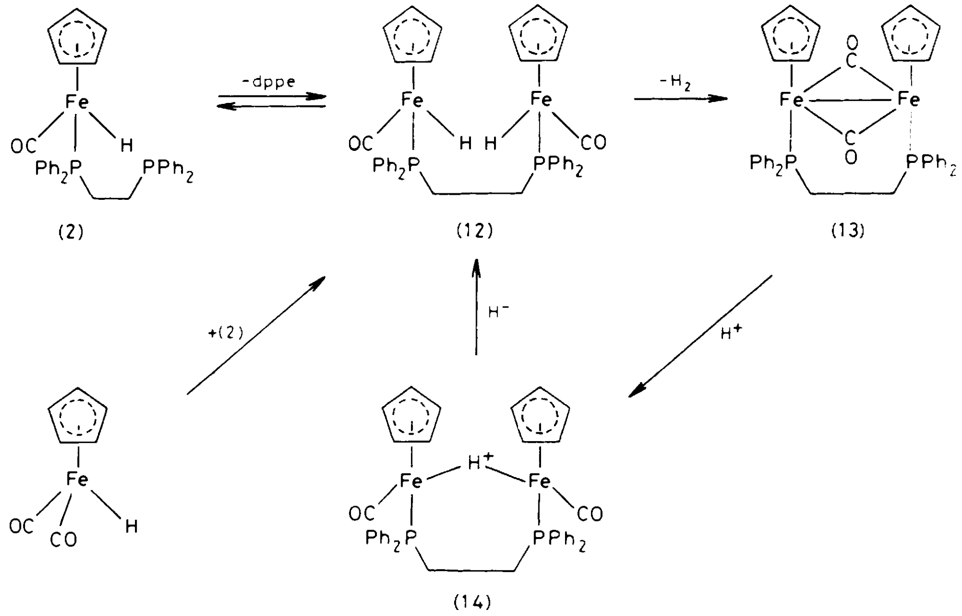
Reduction of cation (1) with $LiAlH_4$ in thf at reflux resulted in the formation of two products: the cyclopentadiene complex (8) and the methyl complex (9) in the ratio 2 : 3. An authentic sample of (9) was prepared by the action of methylmagnesium bromide on $[Fe(\eta^5-C_5H_5)(dppe)Br]$, whose ^{1}H n.m.r. spectrum showed a distinctive methyl triplet at δ −1.3 (J_{PH} = 7 Hz).[21] The novel cyclopentadiene complex (8) was characterised by elemental analysis and high resolution mass spectroscopy. In contrast to the isomeric carbonyl hydride (2), the complex (8) did show the molecular ion (M^+ = 548.111 9) in the mass spectrum. In the 300-MHz ^{1}H n.m.r. spectrum ([$^2H_8$]toluene) of (8), H_{exo} (δ 2.75) and H_{endo} (δ 3.03) could be readily assigned[22] since only H_{exo} exhibited coupling to phosphorus (J_{PH} = 9.3 Hz). The characteristic C–H_{exo} absorption[23] was present at 2 740 cm^{-1} in the i.r. spectrum.

Reduction of cation (1) with $LiAlD_4$ in thf at reflux resulted in formation of the deuteriated compounds (10) and (11). The deuterium in complex (10) was shown to be in the *exo* position by the complete absence of H_{exo} in the ^{1}H n.m.r. spectrum while D_{exo} but no D_{endo} was observed by ^{2}H n.m.r. spectroscopy. In confirmation of this, the C–H_{exo} i.r. absorption was absent for (10) and had been replaced by a D_{exo} absorption at 2 045 cm^{-1}.

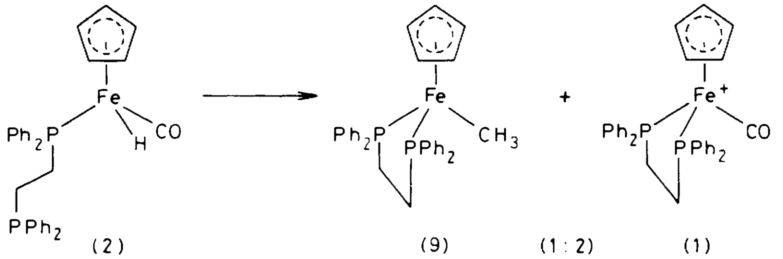
In toluene solution (2) disproportionated *via* phosphine exchange to the known di-iron complex (12)[24] together with free dppe which precipitated from solution on cooling. Treatment of the carbonyl hydride (2) with $[Fe(\eta^5-C_5H_5)(CO)_2H]$ also generated (12). This disproportionation of (2) was reversible since (12) in the presence of excess dppe regenerated (2) and the formation of (12) from (2) could be suppressed by presaturating the toluene with dppe. On warming a toluene solution of (12) to 75 °C in the complete absence of light the formation of the green di-iron complex (13) and an equimolar quantity of hydrogen was observed together with a small amount of $[Fe(\eta^5-C_5H_5)(dppe)H]$ (15). Hydrogen was identified by rotational Raman spectroscopy[25] and an authentic sample of $[Fe(\eta^5-C_5H_5)(dppe)H]$ (15) was prepared by $LiAlH_4$ reduction of $[Fe(\eta^5-C_5H_5)(dppe)Br]$. Photolysis of (12) also produced (13). Under similar conditions (13) is also produced thermally from (2). In the presence of excess dppe, however, to prevent the formation of (12), (2) does not undergo dehydrogenation. Similarly compound (6) is com-



2



3



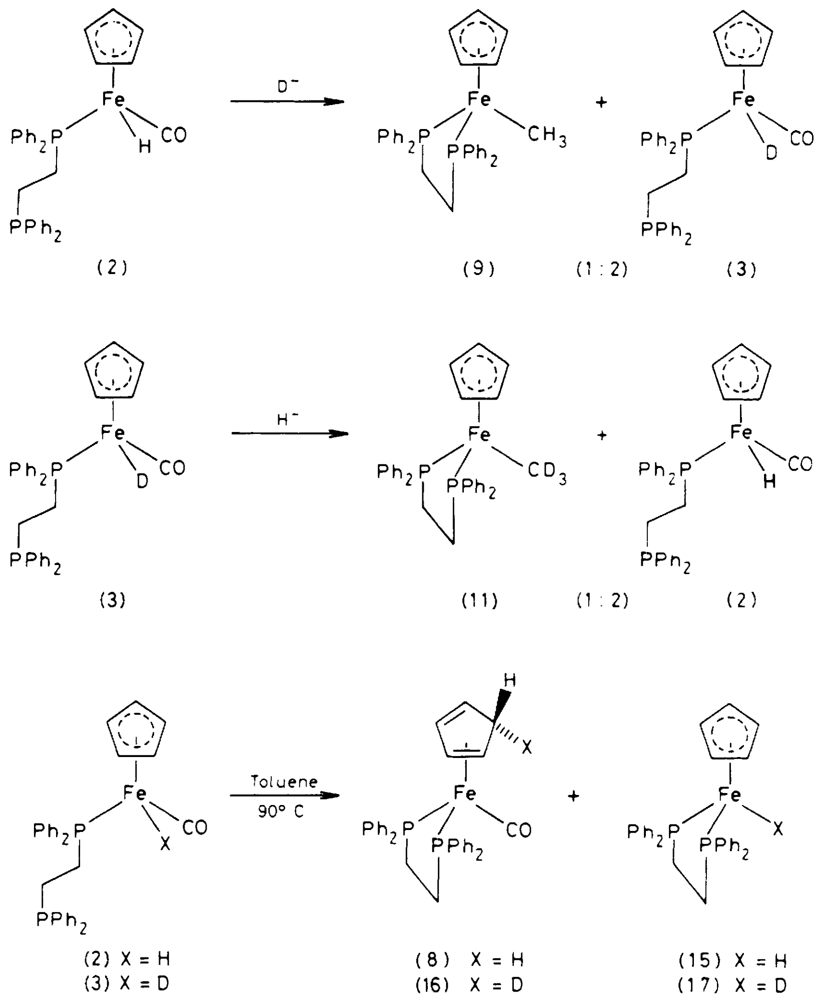
pletely inert to thermolysis. The green di-iron compound (13) could be prepared by thermolysis of $[Fe\{(\eta^5-C_5H_5)(CO)_2\}_2]$ in the presence of dppe. Protonation of (13) gave (14) which on subsequent $LiAlH_4$ reduction produced (12).

Pure carbonyl hydride (2) left at 20 °C for three days produced an oil which contained the characteristic methyl triplet of $[Fe(\eta^5-C_5H_5)(dppe)(CH_3)]$ (9) in its ^1H n.m.r. spectrum. In thf solution (2) disproportionated completely, again with formation of the methyl complex (9) (*ca.* 30% yield) and the cation $[Fe(\eta^5-C_5H_5)(dppe)(CO)]^+$ (1) (*ca.* 60% yield after work-up). Monitoring the reaction mixture by ^{31}P n.m.r. demonstrated that (9) and (1) were the only products produced. The complexes (9) and (1) were readily isolable from this reaction, the latter after anion exchange as its hexafluorophosphate salt.

Under the same conditions but in the presence of $LiAlH_4$, thf solutions of (2) gave after work-up the iron methyl complex (9) and the carbonyl hydride (2) in the ratio 1 : 2. All of the hydrogen atoms in the methyl group of (9) originated from (2) and not from $LiAlH_4$; thus (2) in the presence of $LiAlD_4$ gave after work-up compound (9) and the carbonyl deuteride (3). Similarly (3) in the presence of $LiAlH_4$ gave the CD_3 complex (11) and the carbonyl hydride (2).

Tetrahydrofuran solutions of $[Fe(\eta^5-C_5H_5)(PPh_3)(CO)H]$ (6) in the presence of excess $LiAlH_4$ showed no reaction, (6) being recovered intact.

In contrast to the observed disproportionation reaction of (2) in thf at 20 °C to (9), toluene solutions of (2) containing excess dppe to prevent disproportionation to (12) are indefinitely stable at 20 °C. Thermolysis of (2) in toluene at 90 °C for 20 h in the presence of excess dppe, however, resulted in complete isomerisation to the cyclopentadiene complex (8) together with a small amount ($<5\%$) of $[Fe(\eta^5-C_5H_5)(dppe)H]$ (15). The proportion of (15), formed by loss of carbon monoxide, increased with temperature. Thermolysis of the corresponding carbonyl deuteride (3) under similar conditions



(2) (9) (3)

(3) (11) (2)

(2) X = H
(3) X = D
(8) X = H
(16) X = D
(15) X = H
(17) X = D

resulted in the formation of the D_{endo} cyclopentadiene complex (16) and a small amount of (17). The deuterium in (16) was shown to be in the *endo* position by the complete absence of H_{endo} in the ^1H n.m.r. spectrum while D_{endo} but no D_{exo} was observed by ^2H n.m.r. spectroscopy. In confirmation of this a $C-H_{exo}$ i.r. absorption was present for (16) at 2 740 cm^{-1} together with a $C-D_{endo}$ absorption at 2 170 cm^{-1}.

Monitoring the rearrangement of (2) to (8) showed it to be first order, $k_{348} = 1.60 \times 10^{-4}$ s^{-1}, $\Delta G_{348}^{\ddagger} = 26.5$ kcal mol^{-1}. Similarly the rearrangement of (3) to (16) proceeded with a rate constant $k_{348} = 1.65 \times 10^{-4}$ s^{-1}, showing the isotope effect k_H/k_D to be unity within experimental error.

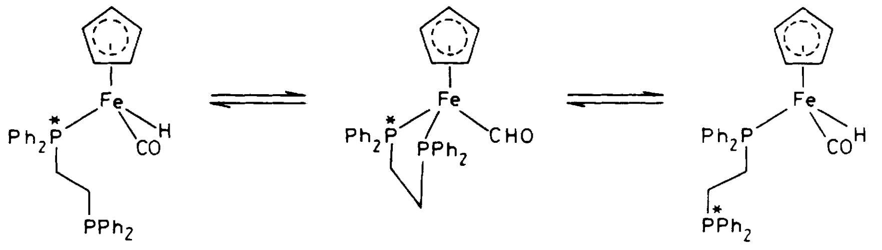
Discussion

The formation of the carbonyl hydride (2) by nucleophilic hydride addition to the cation of (1) at −78 °C proceeds either by direct attack on the metal after prior dissociation of a two-electron ligand [20] or *via* initial attack on the carbonyl ligand followed by hydrogen migration from the formyl thus produced to the metal. The third alternative, *exo* attack on the cyclopentadienyl ring with subsequent transfer of the *endo* hydrogen to the metal is incompatible with the observed formation of the metal deuteride (3) corresponding to (2) when (1) is reduced with $LiAlD_4$. The observation of the formyl (4) in the ^1H n.m.r. spectrum of the reaction mixture is consistent with direct attack onto co-ordinated carbon monoxide.

Although hydride reduction of cation (1) occurs regiospecifically at the carbonyl at low temperatures, at elevated temperatures regiospecificity is lost and *exo* attack onto the cyclopentadienyl ligand competes with attack at the carbonyl. Stereospecific attack *exo* onto the cyclopentadienyl ligand was confirmed by deuterium labelling studies.

The formation of (2) *via* the formyl (4) suggested the possibility that these two compounds might be in equilibrium at room temperature. Such an equilibrium is considered to be an essential feature of the Fischer–Tropsch and related reactions. ^{31}P N.m.r. saturation transfer experiments clearly demonstrated that the co-ordinated and unco-ordinated phosphorus atoms in (2) but not in (7) were rapidly equilibrating. Exchange with external dppe was not observed under these conditions. Exchange *via* the formyl (4) is the only possible mechanism available to (2) that is unavailable to (7) (Scheme 1). The value of $\Delta G_{298}^{\ddagger}$ (18 kcal mol^{-1}) for this exchange would therefore represent the maximum value in this case for the energy difference between a metal carbonyl hydride and metal phosphine formyl.

The precise evaluation of this energy difference has been the subject of much effort. The lower limit has been put at 3 kcal mol^{-1}, this value corresponding to the ^1H n.m.r. detection limit of 1% of a formyl species *in equilibrium* with its metal hydride. Unfortunately this *equilibrium* has never been directly observed despite considerable effort.[7] Consideration of thermodynamic cycles comparing the well known insertion of CO into metal–carbon bonds and the unknown insertion of CO into metal–hydrogen bonds leads to the conclusion that the relative thermochemistry of metal acyl and metal formyl formation is determined largely by the difference in metal–

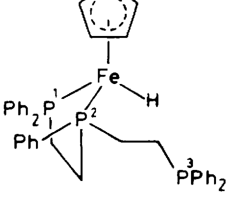


(2) (4) (2)

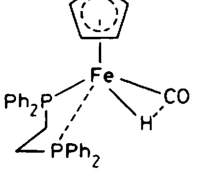
Scheme 1. Phosphorus exchange mechanism

hydrogen (~ 60 kcal mol^{-1}) and metal–carbon (~ 30 kcal mol^{-1}) bond energies.[5] Metal-acyl formation is generally favoured by *ca.* 10 kcal mol^{-1}, thus we can see that metal–formyl formation is disfavoured by *ca* 20 kcal mol^{-1}. The demonstrated equilibrium (2) $\rightleftharpoons$ (4) has in its favour the entropic factor associated with chelation of the free phosphine in (2) to form (4), thus this particular case would be expected to be disfavoured by an energy substantially lower than 20 kcal mol^{-1}, but in the absence of the value of this entropic factor, this barrier cannot be evaluated.

The P–P coupling constants observed in the hydride (7) are $J_{P^1P^2}$ = 28 and $J_{P^2P^3}$ = 35 Hz. These are consistent with the expected thermodynamically most stable *anti* conformation being adopted by P^2 and P^3 (dihedral angle 180°) while the dihedral angle between P^1 and P^2 will be 25—50° (see Table 2) with an expected P–P coupling constant of 30—40 Hz.[26] Similarly for the cation [Fe(η^5-C_5H_5)(CO)$_2$(dppe)]$^+$ J_{PP} = 38 Hz.[27] In contrast for hydride (2) the P–P coupling constant is close to zero implying that in [Fe(η^5-C_5H_5)(dppe)(CO)H] (2) the dihedral angle is approximately 90°. The inherent thermodynamic disadvantage in such a conformation is presumably compensated for by a metal–phosphorus interaction suggesting that (18) might be a better representation of the structure [Fe(η^5-C_5H_5)(dppe)(CO)H] than (2).



(7)



(18)

Table 2. Torsion angles about the C–C bond of co-ordinated dppe

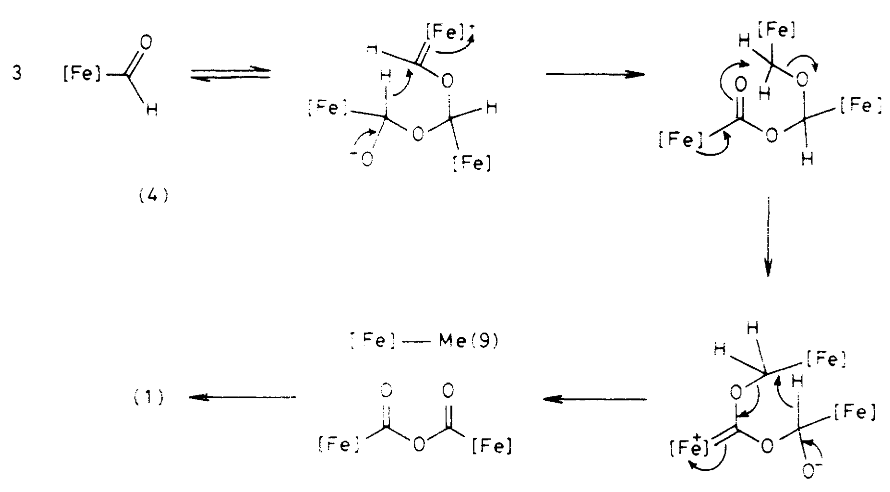
	τ(C–C)	Ref.
[Fe(η^5-C_5H_5)(MeCN)(dppe)]$^+$	48.4	*a*
[Fe(η^5-C_5H_5)(CO)(dppe)]$^+$	42.8	*b*
[Fe(η^5-C_5H_5)(COC_6H_5)(dppe)]	36.1	*c*
[Fe(η^5-C_5H_5){MgBr(thf)$_2$}(dppe)]	25.4	*d*
[Nb(η^5-C_5H_5)Cl_3(dppe)]	62.3	*e*
[ReH_3(PPh_3)(dppe)]	55.0	*f*
[$PdCl_2$(dppe)]	50.1	*g*

[a] P. E. Riley, C. E. Capshew, R. Pettit, and R. E. Davis, *Inorg. Chem.*, 1978, **17**, 408. [b] P. E. Riley and R. E. Davis, *Organometallics*, 1983, **2**, 286. [c] H. Felkin, B. Meunier, C. Pascard, and T. Prange, *J. Organomet. Chem.*, 1977, **135**, 361. [d] H. Felkin, P. J. Knowles, B. Meunier, A. Mitschler, L. Ricard, and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 1974, 44. [e] J. C. Daran, K. Prout, A. DeCian, M. L. H. Green, and N. Siganporia, *Acta Crystallogr., Sect. B*, 1979, **35**, 2882. [f] V. Albano, P. Bellon, and V. Scatturin, *Rend. Ist. Lomb. Acad. Sci. Lett. A.*, 1966, **100**, 989. [g] W. L. Steffer and G. J. Polensk, *Inorg. Chem.*, 1976, **15**, 2432.

In toluene solution the carbonyl hydride (2) is in equilibrium with the di-iron dihydride (12) and free dppe. Removal of dppe by cooling leads to complete conversion to (12) whereas saturation of the toluene solution with dppe prevents formation of (12). Dihydride (12) produces the green di-iron species (13) and hydrogen on thermolysis or photolysis. Complex (13) could be reconverted to (12) *via* sequential protonation and hydride reduction. Loss of dihydrogen from (12) is apparently intramolecular in nature since neither (2) nor (6) loses dihydrogen under similar conditions. Compound (12) is both co-ordinatively and electronically saturated and thus is unable to form a bridging hydride intermediate which could lead to elimination from one metal centre in a dinuclear species. This suggests that dihydrogen is eliminated from (12) in a synchronous manner involving both metal centres. It is recognised that (12) contains two chiral iron centres and therefore two diastereoisomers should exist. The three methods used to generate (12) all gave the same single compounds by ^1H, ^{31}P, and ^{13}C n.m.r. It is unlikely that all three preparations would be stereoselective and therefore the two diastereoisomers are probably equilibrating rapidly on the n.m.r. time-scale. Attempts to ' freeze out ' the two diastereoisomers at −80 °C have been unsuccessful. The analogous diruthenium dihydride complex does exhibit distinguishable diastereoisomers.[28]

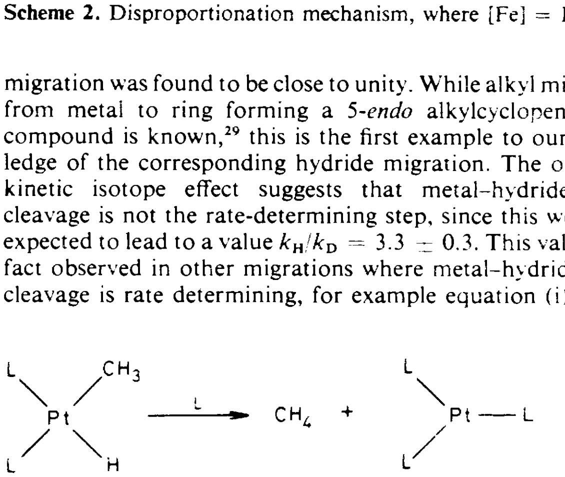
In contrast to the behaviour of (2) in the non-polar solvent toluene, in thf it disproportionates to the methyl complex (9) and cation (1) (1 : 2). In the presence of $LiAlH_4$ (1) is reconverted to hydride (2). Complete conversion of all the iron species present to the methyl complex (9) is not observed, consistent with the initial reduction of cation (1) exclusively giving the carbonyl hydride (2) with no further reduction to methyl being observed even after prolonged reaction times in the presence of excess $LiAlH_4$. Presumably in both cases co-ordination of the unbound phosphine to AlH_3 prevents equilibration with formyl (4) and hence further reduction. Metal formyls have been reported to disproportionate to the corresponding hydroxymethyl and carbonyl cation, however complete reduction to methyl generally requires a Lewis acid and an external hydride source.[5,6] A mechanism for the disproportionation of (2) to (9) by analogy with aldehyde trimerisations and the Cannizzaro and related hydride transfer reactions is given in Scheme 2.

Thermolysis of the carbonyl hydride (2) in toluene in the presence of excess dppe to prevent formation of (12) results in the rearrangement of (2) to the cyclopentadiene complex (8). Deuterium labelling and kinetic data confirm this to be a first-order reaction with hydrogen migrating from the metal to the *endo* position on cyclopentadiene. The isotope effect for this



Scheme 2. Disproportionation mechanism, where [Fe] = Fe(η^5-C_5H_5)(dppe)

migration was found to be close to unity. While alkyl migration from metal to ring forming a 5-*endo* alkylcyclopentadiene compound is known,[29] this is the first example to our knowledge of the corresponding hydride migration. The observed kinetic isotope effect suggests that metal–hydride bond cleavage is not the rate-determining step, since this would be expected to lead to a value $k_H/k_D = 3.3 \pm 0.3$. This value is in fact observed in other migrations where metal–hydride bond cleavage is rate determining, for example equation (i).[30] It is therefore likely that metal–phosphine bond formation may be the rate-determining step in the conversion of (2) to (8) presumably *via* an η^3-cyclopentadienyl intermediate.



(i)

L = PPh$_3$

Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum-line and Schlenk-tube techniques.[31] Tetrahydrofuran and toluene were dried over sodium benzophenone ketyl and distilled. Diethyl ether and light petroleum (b.p. 40—60 °C) were dried over sodium wire and distilled. Dichloromethane was dried over calcium hydride and distilled. Dimethyl sulphoxide was dried over lithium aluminium hydride and distilled. Infrared spectra were recorded on a Perkin-Elmer 297 instrument. Nuclear magnetic resonance spectra were recorded on Perkin-Elmer R12B (60 MHz, ^{1}H), Varian EM360L (60 MHz, ^{1}H), Bruker WH90 (90 MHz, ^{1}H; 36.43 MHz, ^{31}P), and Bruker WH300 (300, ^{1}H; 121.49, ^{31}P; 75.47, ^{13}C; 46.07 MHz, ^{2}H) spectrometers. Magnetisation transfer experiments were carried out on the WH300 instrument using the DANTE pulse sequence [19] to generate selective 180° pulses. Mass spectra were recorded on a VG Micromass ZAB 1F instrument using the field-desorption technique. The accurate mass measurement was obtained by the in-beam electron impact technique. Elemental analyses were performed by the Central Microanalytical Service of the C.N.R.S., France, and Dr. F. B. Strauss, Oxford. Chromatography was performed on alumina (Grade IV/V) under nitrogen.

Preparations and Reactions.—[Fe(η^5-C_5H_5)(dppe)(CO)]PF$_6$ (1). A mixture of [Fe(η^5-C_5H_5)(CO)$_2$Br] (2.0 g, 7.8 mmol) and dppe (3.2 g, 8.0 mmol) was heated under reflux in toluene (75 cm^3) for 2 h. Cooling and filtration gave a yellow solid which was washed with toluene (2 × 30 cm^3) and suspended in wet acetone (60 cm^3) containing NH_4PF_6 (2.2 g, 13.5 mmol). $Me_3NO \cdot 2H_2O$ (1.0 g, 9.0 mmol) was added and the mixture stirred for 1 h. Removal of the solvent under reduced pressure and extraction with CH_2Cl_2 (2 × 50 cm^3) gave a yellow-green solution which was washed with distilled water (40 cm^3) decanted, and dried over calcium chloride. Filtration, concentration (15 cm^3), and slow addition of diethyl ether gave on cooling (−30 °C) yellow crystals of (1), 4.9 g (90%); $\nu_{max.}$ (Nujol) 1 980s (CO) cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2CO$] δ 8.0—7.2 (20 H, m, aryl-H), 5.08 (5 H, t, J_{PH} = 1 Hz, C_5H_5), and 3.0—2.7 (4 H, m, CH_2); ^{31}P-{^{1}H} n.m.r. (acetone) δ 92.0; ^{13}C-{^{1}H} n.m.r. [$(CD_3)_2CO$] δ 213.8 (t, J_{PC} = 26.5 Hz, CO), 135.7—129.0 (m, aryl-C), 84.8 (s, C_5H_5), and 28.4 (m, CH_2); m/z 547 $[M]^+$.

[Fe(η^5-C_5H_5)(dppe)(CO)H] (2). A solution of [Fe(η^5-C_5H_5)(dppe)(CO)]PF$_6$ (1) (3.1 g, 4.5 mmol) in thf-dichloromethane (1 : 1, 80 cm^3) was cooled (−78 °C) with stirring. $LiAlH_4$ (0.5 g, 13 mmol) was added and the mixture stirred for 2 h at −78 °C. Storage at −30 °C with occasional agitation (10 h) gave an orange solution which was treated with water (1 cm^3) and allowed to warm to 20 °C. Removal of the solvent under reduced pressure and extraction with diethyl ether (2 × 60 cm^3) gave a yellow solution which on concentration and cooling (−78 °C) gave (2) as a yellow microcrystalline solid, 1.84 g (75%) (Found: C, 70.1; H, 5.7; P, 11.6. $C_{32}H_{30}FeOP_2$ requires C, 70.1; H, 5.5; P, 11.3%); $\nu_{max.}$ (Nujol) 1 910s (CO) and 1 880w (Fe–H) cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ 7.7—6.6 (20 H, m, aryl-H), 4.15 (5 H, d, J_{PH} = 1 Hz, C_5H_5), 2.7—2.1 (4 H, m, CH_2), and −13.23 (1 H, d, J_{PH} = 74 Hz, FeH); ^{31}P-{^{1}H} n.m.r. (C_6H_6) δ 84.8 (s, Fe–P) and −13.5 (s, $FePCH_2CH_2P$); m/z 547 $[M - 1]^+$.

[Fe(η^5-C_5H_5)(dppe)(CO)D] (3). This was prepared by a similar method to that above for (2) using $LiAlD_4$ followed by D_2O (yield 70%). The product contained less than 1% of the protio-compound (2) as shown by ^{1}H n.m.r. and no detectable deuterium incorporation into the η^5-C_5H_5 or dppe ligands as shown by ^{2}H n.m.r. [^{2}H n.m.r. (toluene) δ −13.2 (d, J_{PD} = 11.4 Hz)].

[Fe(η^5-C$_5$H$_5$)(PPh$_3$)$_2$(CO)]PF$_6$ (5). A mixture of [Fe(η^5-C$_5$H$_5$)(PPh$_3$)(CO)$_2$]PF$_6$ (2.0 g, 3.43 mmol), triphenylphosphine (1.0 g, 3.82 mmol), and Me$_3$NO·2H$_2$O (0.84 g, 7.50 mmol) in acetone was stirred for 1 h at 20 °C. The solvent was removed under reduced pressure and the orange residue extracted with dichloromethane (3 × 20 cm^3) and concentrated (5 cm^3). Chromatography [dichloromethane–toluene (1 : 1)] gave an orange band which on evaporation gave orange crystals of (5), 2.0 g (70%); $\nu_{max.}$ (Nujol) 1 980s (CO) cm^{-1}; ^{1}H n.m.r. [(CD$_3$)$_2$CO] δ 7.4—6.9 (30 H, m, aryl-H) and 4.80 (5 H, t, J_{PH} = 1 Hz, C$_5$H$_5$); ^{31}P-{^{1}H} n.m.r. (CH$_2$Cl$_2$) δ 56.6.

[Fe(η^5-C$_5$H$_5$)(PPh$_3$)(CO)H] (6). A solution of [Fe(η^5-C$_5$H$_5$)(PPh$_3$)$_2$(CO)]PF$_6$ (5) (0.2 g, 0.25 mmol) in thf–dichloromethane (1 : 1; 30 cm^3) was cooled (−78 °C) with stirring. LiAlH$_4$ (0.1 g, 2.6 mmol) was added and the mixture warmed to 20 °C; the orange-yellow mixture became yellow on stirring for 10 min at 20 °C. After dropwise addition of H$_2$O (1 cm^3) at −78 °C, the reactants were warmed to 20 °C and the solvents removed under reduced pressure. Extraction into diethyl ether (3 × 10 cm^3), concentration (5 cm^3), and filtration through alumina (5 cm) gave a bright yellow solution which on evaporation gave (6) as a yellow powder, 0.075 g (74%); $\nu_{max.}$ (hexane) 1 930s (CO) cm^{-1}; ^{1}H n.m.r. (C$_6$D$_6$) δ 7.7—6.9 (15 H, m, aryl-H), 4.20 (5 H, d, J_{PH} = 1 Hz, C$_5$H$_5$), and −12.72 (1 H, d, J_{PH} = 74 Hz, Fe–H).

[Fe(η^5-C$_5$H$_5$)(PPh$_3$)(CO)D] (6a). The method was analogous to that used above for (6) using LiAlD$_4$ followed by D$_2$O (yield 84%). The product contained less than 1% of the protio-compound (6) as shown by ^{1}H n.m.r. and no detectable deuterium incorporation into the η^5-C$_5$H$_5$ moiety as shown by ^{2}H n.m.r.; $\nu_{max.}$ (benzene) 1 915s (CO) cm^{-1}; ^{1}H n.m.r. (C$_6$D$_6$) δ 7.7—6.9 (15 H, m, aryl-H) and 4.25 (5 H, d, J_{PH} = 1 Hz, C$_5$H$_5$); ^{2}H n.m.r. (benzene) δ −12.8 (d, J_{PD} = 11.4 Hz); ^{31}P-{^{1}H} n.m.r. (benzene) δ 56.6 (t, J_{PD} = 11.0 Hz); *m/z* 413 [*M*]$^+$.

Low-temperature generation of [Fe(η^5-C$_5$H$_5$)(dppe)(CHO)] (4). A saturated solution of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)]PF$_6$ (1) in [^{2}H$_8$]thf (0.6 cm^3) at −80 °C was filtered into an n.m.r. tube containing LiAlH$_4$ (3 mg). The reactants were kept at −78 °C for 1 h and then transferred to the pre-cooled probe of the Bruker WH90 spectrometer. Monitoring the ^{1}H n.m.r. spectrum as the temperature was slowly raised showed the presence of a resonance at δ 11.53 at temperatures between −70 and −50 °C.

A similar experiment using LiBEt$_3$H in place of LiAlH$_4$ gave the same results.

[{Fe(η^5-C$_5$H$_5$)(μ-CO)}$_2$(μ-dppe)] (13).[32] A mixture of [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] (7.98 g, 22.5 mmol) and dppe (13.69 g, 34.4 mmol) in toluene (60 cm^3) was heated under reflux (6 h). The resulting dark green solution was cooled and evaporated under reduced pressure. The green mass was triturated with diethyl ether (3 × 30 cm^3) and the remaining solid recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to give (13) as dark green microcrystals, 11.1 g (71%); $\nu_{max.}$ (Nujol) 1 690s (CO) and 1 670m (CO) cm^{-1}; ^{1}H n.m.r. (C$_6$D$_6$) δ 8.0—6.8 (20 H, m, aryl-H), 4.23 (10 H, s, C$_5$H$_5$), and 1.4—1.1 (4 H, m, CH$_2$); ^{31}P-{^{1}H} n.m.r. (benzene) δ 68.7; *m/z* 696 [*M*]$^+$.

[{Fe(η^5-C$_5$H$_5$)(CO)}$_2$(μ-dppe)(μ-H)]BF$_4$ (14).[33] A solution of [{Fe(η^5-C$_5$H$_5$)(μ-CO)}$_2$(μ-dppe)] (13) (1.0 g, 0.15 mmol) in dichloromethane (20 cm^3) was stirred vigorously at 0 °C. HBF$_4$·OMe$_2$ (0.2 cm^3, 1.6 mmol) was added, followed by the slow addition of diethyl ether (80 cm^3) to give green microcrystalline (14) which was filtered off, washed with diethyl ether (2 × 20 cm^3), and dried *in vacuo*, 1.0 g (92%); $\nu_{max.}$ (Nujol) 1 940s (CO) cm^{-1}; ^{1}H n.m.r. (CD$_2$Cl$_2$) δ 7.6—6.7 (20 H, m, aryl-H), 4.1 (10 H, s, C$_5$H$_5$), 2.4—2.1 (4 H, m, CH$_2$), and −36.9 (1 H, t, J_{PH} = 26 Hz, Fe–H–Fe); ^{31}P-{^{1}H} n.m.r. (CH$_2$Cl$_2$) δ 66.1; *m/z* 697 [*M*]$^+$.

[{Fe(η^5-C$_5$H$_5$)(CO)H}$_2$(μ-dppe)] (12). *Method A*. A solution of [{Fe(η^5-C$_5$H$_5$)(CO)}$_2$(μ-dppe)(μ-H)]BF$_4$ (14) (1.2 g, 1.53 mmol) in thf (50 cm^3) was cooled (−78 °C) prior to the addition of LiAlH$_4$ (0.2 g, 5.2 mmol). The suspension was stirred at −78 °C for 1 h, warmed to 20 °C and stirred for a further 8 h. Dropwise addition of water (1 cm^3) and removal of solvent under reduced pressure left a yellow-green residue which was extracted with toluene (2 × 50 cm^3). The extracts were combined, concentrated (10 cm^3), and chromatographed (toluene). The yellow fraction first eluted was evaporated. Recrystallisation from diethyl ether–light petroleum (1 : 4; −30 °C) gave (12), 0.73 g (68%); $\nu_{max.}$ (Nujol) 1 915s (CO) and 1 870w (Fe–H) cm^{-1}; ^{1}H n.m.r. (C$_6$D$_6$) δ 7.4—6.6 (20 H, m, aryl-H), 3.9 (10 H, s, C$_5$H$_5$), 2.4—2.2 (4 H, m, CH$_2$), and −13.35 (2 H, d, J_{PH} = 74 Hz, Fe–H); ^{31}P-{^{1}H} n.m.r. (C$_6$H$_6$) δ 84.4; ^{13}C-{^{1}H} n.m.r. [(CD$_3$)$_2$CO] δ 221.6 (d, J_{PC} = 27.5 Hz, CO), 140.0—128.5 (m, aryl), 80.7 (s, C$_5$H$_5$), and 28.4 (m, CH$_2$); *m/z* 696 [*M* − 2]$^+$.

The green fraction eluted second was identified as (13) by comparison with an authentic sample.

Method B. A solution of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2) (1.59 g, 2.9 mmol) in acetone or toluene (3 cm^3) was frozen in liquid nitrogen and rapidly thawed three times. A white precipitate was observed and the solution rapidly filtered cold (*ca.* −50 °C). Removal of the solvent under reduced pressure gave (12) as a bright yellow solid (0.71 g, 70%).

Method C.[34] A solution of [Fe(η^5-C$_5$H$_5$)(CO)$_2$Cl] (0.59 g, 0.28 mmol) in diethyl ether (20 cm^3) was cooled (−78 °C) prior to the addition of LiAlH$_4$ (0.02 g, 0.52 mmol). Warming to 0 °C and stirring (2 h) gave a pale brown solution of [Fe(η^5-C$_5$H$_5$)(CO)$_2$H] and [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$]. The complex [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2) (0.22 g, 0.39 mmol) was added to this solution which was then stirred at 0 °C for 4 h. Addition of water (1 cm^3) and evaporation under reduced pressure gave a red residue which was extracted with toluene (2 × 20 cm^3), concentrated, and chromatographed (toluene). Evaporation of the yellow fraction and recrystallisation as above gave (12) (0.10 g, 52%).

[Fe(η^5-C$_5$H$_5$)(dppe)H] (15). LiAlH$_4$ (0.2 g, 5.2 mmol) was added to a stirred solution of [Fe(η^5-C$_5$H$_5$)(dppe)Br] (0.65 g, 1.09 mmol) in thf (50 cm^3) at −78 °C. After stirring for 4 h at −78 °C the reactants were allowed to warm to 0 °C and water (0.5 cm^3) was added. Evaporation, extraction with light petroleum (2 × 40 cm^3), concentration, and cooling (−30 °C) gave (15) as orange-red crystals, 0.32 g (57%); $\nu_{max.}$ (Nujol) 1 860m (Fe–H) and 1 820m (Fe–H) cm^{-1}; ^{1}H n.m.r. (C$_6$D$_6$) δ 8.0—6.8 (20 H, m, aryl-H), 4.15 (5 H, s, C$_5$H$_5$), 2.3—1.7 (4 H, m, CH$_2$), and −16.1 (1 H, t, J_{PH} = 75 Hz, Fe–H); ^{31}P-{^{1}H} n.m.r. (C$_6$H$_6$) δ 110.3.

Thermolysis of [{Fe(η^5-C$_5$H$_5$)(CO)H}$_2$(μ-dppe)] (12). A solution of (12) (0.65 g, 0.93 mmol) in toluene (10 cm^3) was filtered into an ampoule with a side-arm suitable for monitoring gas rotational Raman spectra. The vessel was cooled (−196 °C), evacuated, and sealed. After heating in the absence of light (90 °C) for 20 h a deep green solution was obtained. Direct analysis of the gas above the solution by Raman spectroscopy showed the two strong lines characteristic of hydrogen at 358 and 591 cm^{-1} (lit.[25] 345 and 586 cm^{-1}) in the ratio 1 : 3. The volume of hydrogen was measured by standard techniques [31] as 15.2 cm^3 (s.t.p.). The solution was monitored by ^{31}P n.m.r. which demonstrated the presence of [Fe(η^5-C$_5$H$_5$)(dppe)H] (15) and [{Fe(η^5-C$_5$H$_5$)(μ-CO)}$_2$(μ-dppe)] (13) at δ 110.3 and 68.8 respectively in the ratio 1 : 3. The yield of hydrogen from the conversion of (12) to (13) was thus 96% (±5%). Pure (13) was isolated from the reaction mixture by chromatography (toluene) and crystallisation from diethyl ether–light petroleum (1 : 4) as green needles, 0.37 g (57%).

Thermolysis at 75 °C resulted in (15) being observed in less than 5% yield. Increasing the reaction temperature increased the proportion of (15).

Thermolysis of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2). A solution of (2) (0.1 g, 0.18 mmol) in toluene (20 cm^3) was heated (90 °C) in the absence of light (16 h) during which time the initially orange solution became dark green. Chromatography (toluene) gave a green fraction. Evaporation and crystallisation as above gave green crystals of (13) identified by comparison with an authentic sample.

Photolysis of [{Fe(η^5-C$_5$H$_5$)(CO)H}$_2$(μ-dppe)] (12). A solution of (12) (0.1 g, 0.14 mmol) in [^{2}H$_6$]benzene (0.7 cm^3) was photolysed at 20 °C for 35 h with a 50-W tungsten filament bulb. Analysis of the reaction mixture by ^{1}H and ^{31}P n.m.r. spectroscopy showed the presence of both (15) and (13) in the ratio 1 : 3. Evaporation and crystallisation as above gave (13), 0.05 g (49%).

[Fe(η^4-C$_5$H$_6$)(dppe)(CO)] (8). A solution of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2) (0.68 g, 1.24 mmol) in toluene (40 cm^3) was saturated with dppe (*ca.* 5 g) at 20 °C. The reactants were heated (80 °C) in the absence of light (8 h). Removal of the solvent under reduced pressure and extraction with light petroleum (3 × 40 cm^3) gave an orange solution. Concentration (15 cm^3) and chromatography (toluene–light petroleum; 2 : 3) gave after evaporation an orange powder which was dissolved in acetone (30 cm^3), filtered, and concentrated (15 cm^3). Cooling (−30 °C) gave large colourless blocks of dppe. The supernatant was concentrated (10 cm^3) and recooled (−30 °C) to yield a further small amount of dppe. The orange filtrate was evaporated to dryness and recrystallised from diethyl ether (−30 °C) to give bright orange microcrystalline (8), 0.33 g (49%) (Found: C, 70.10; H, 5.60; P, 10.75. C$_{32}$H$_{30}$FeOP$_2$ requires C, 70.05; H, 5.45; P, 11.30%); $\nu_{max.}$ (Nujol) 2 740m (CH$_{exo}$) and 1 880s (CO); ^{1}H n.m.r. (C$_6$D$_6$) δ 7.8—6.9 (20 H, m, aryl-H), 4.89 (2 H, s, H^{2,3}), 3.03 (1 H, d, J_{HH} = 10.0 Hz, H$_{endo}$), 2.75 (1 H, dt, J_{HH} = 10 Hz, J_{PH} = 9.3 Hz, H$_{exo}$), 2.43 (2 H, s, H^{1,4}), and 2.1—1.8 (4 H, m, CH$_2$); ^{31}P-{^{1}H} n.m.r. (acetone) δ 91.8; *m/z* (Found: 548.1119. C$_{32}$H$_{30}$FeOP$_2$ requires 548.1121).

[Fe(5-*endo*-η^4-C$_5$H$_5$D)(dppe)(CO)] (16). This compound was prepared from [Fe(η^5-C$_5$H$_5$)(dppe)(CO)D] (3) as described above for the protio-compound (8) in 40% yield; $\nu_{max.}$ (Nujol) 2 740w (CH$_{exo}$), 2 170w (CD$_{endo}$), and 1 880s (CO); ^{2}H n.m.r. (C$_6$H$_6$) δ 3.01 (br, *D*$_{endo}$).

Kinetics of the migration of (2) *to* (8) *and* (3) *to* (16). Solutions of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2) and [Fe(η^5-C$_5$H$_5$)(dppe)(CO)D] (3) in toluene were prepared at identical concentrations (0.13 g in 3 cm^3, 0.08 mol dm^{-3}) and were saturated with dppe prior to filtration into 8-mm n.m.r. tubes. The samples were in turn equilibrated in the probe of the Bruker WH90 instrument (30 min) and ^{31}P n.m.r. spectra were then acquired every 10 min for at least two half lives. The probe temperature for these consecutive experiments was 75 ±1 °C, determined by use of the ^{31}P chemical shift thermometer.[35] The extent of the decarbonylation reaction leading to [Fe(η^5-C$_5$H$_5$)(dppe)H] (15) was less than 5% at this temperature. The conversions were found to obey first-order kinetics with the rate constants $k_H = 1.60\ (\pm 0.05) \times 10^{-4}$ s^{-1} and $k_D = 1.65\ (\pm 0.05) \times 10^{-4}$ s^{-1}.

[Fe(η^5-C$_5$H$_5$)(dppe)(CH$_3$)] (9). A solution of [Fe(η^5-C$_5$H$_5$)(dppe)Br] (0.47 g, 0.78 mmol) in thf (20 cm^3) was cooled to 0 °C. Methylmagnesium bromide (2 cm^3, 0.8 mol dm^{-3}, 1.6 mmol) was added dropwise and the reactants stirred at 0 °C for 5 h. Addition of water (1 cm^3) and removal of the solvent under reduced pressure gave a red oil which was extracted with toluene (2 × 20 cm^3). Evaporation and crystallisation from dichloromethane–light petroleum gave red rod-like crystals of (9), 0.18 g (43%); ^{1}H n.m.r. (CS$_2$), δ 7.7—7.0 (20 H, m, aryl-H), 3.8 (5 H, s, C$_5$H$_5$), 2.2—1.8 (4 H, m, CH$_2$), and −1.3 (3 H, t, J_{PH} = 7 Hz, Fe–CH$_3$); ^{31}P-{^{1}H} n.m.r. (CS$_2$) δ 110.6; *m/z* 534 [*M*]$^+$.

Disproportionation of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2). *Method A.* Complex (2) was left at 20 °C for 3 d. The yellow-orange powder slowly transformed to a deep red oil and a ^{1}H n.m.r. spectrum of the crude material (CS$_2$) showed substantial amounts of the compound [Fe(η^5-C$_5$H$_5$)(dppe)(CH$_3$)] (9) to be present as identified by the characteristic high-field signal at δ −1.3 (t, J_{PH} = 7 Hz, Fe–CH$_3$).

Method B. A solution of (2) (0.6 g, 1.09 mmol) in thf (30 cm^3) was allowed to stand at 20 °C for 3 d. A ^{31}P-{^{1}H} n.m.r. spectrum of the crude thf solution showed the presence of (9) and (1) only. The solvent was removed from the resulting deep orange-red solution under reduced pressure. Extraction with diethyl ether (2 × 30 cm^3) and evaporation gave deep red crystals of [Fe(η^5-C$_5$H$_5$)(dppe)(CH$_3$)] (9), 0.17 g (30%). The yellow-orange residue remaining was stirred with NH$_4$PF$_6$ (1.0 g, 6.1 mmol) in wet acetone (30 cm^3) for 30 min. Evaporation and crystallisation from dichloromethane–diethyl ether gave yellow crystals of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)]PF$_6$ (1), 0.47 g (62%). The yield and products were unaffected by carrying out the reaction in the absence of light.

Disproportionation of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2) *in the presence of* LiAlD$_4$. A solution of (2) (0.26 g, 0.47 mmol) in thf (30 cm^3) was cooled to 0 °C prior to the addition of LiAlD$_4$ (0.2 g, 5.2 mmol). The mixture was stirred at 20 °C for 3 d. The deep orange solution was cooled (0 °C), treated with water (1 cm^3) and evaporated. The residue was extracted with diethyl ether (2 × 30 cm^3) and removal of the solvent from the extracts gave a deep red oily solid. A combination of ^{1}H, ^{2}H, and ^{31}P n.m.r. spectroscopy showed the presence of [Fe(η^5-C$_5$H$_5$)(dppe)(CH$_3$)] (9) and [Fe(η^5-C$_5$H$_5$)(dppe)(CO)D] (3) as the sole products in the ratio 1 : 2. The isotopic purity by n.m.r. spectroscopy of each product was >98% and mass spectrometry confirmed this.

In an identical experiment [Fe(η^5-C$_5$H$_5$)(dppe)(CO)D] (3) was stirred with LiAlH$_4$. The sole products were [Fe(η^5-C$_5$H$_5$)(dppe)(CD$_3$)] (11) and [Fe(η^5-C$_5$H$_5$)(dppe)(CO)H] (2) in the ratio 1 : 2 with isotopic purities of >98%.

Treatment of [Fe(η^5-C$_5$H$_5$)(PPh$_3$)(CO)H] (6) *with* LiAlH$_4$. A solution of (6) (0.2 g, 0.49 mmol) and LiAlH$_4$ (0.1 g, 2.6 mmol) in thf (40 cm^3) was stirred at 20 °C for 3 d. Hydrolysis and work-up led to the recovery of (6) only.

High temperature reduction of [Fe(η^5-C$_5$H$_5$)(dppe)(CO)]PF$_6$ (1). A suspension of (1) (1.0 g, 1.45 mmol) in thf (50 cm^3) was heated under reflux. Addition of LiAlH$_4$ (0.22 g, 5.79 mmol) caused immediate formation of an orange solution which was stirred under reflux for 15 min. The solution was rapidly cooled (0 °C) and hydrolysed (1 cm^3). Removal of solvent under reduced pressure and extraction with diethyl ether (2 × 30 cm^3) gave a deep red solution from which deep red blocks were obtained on removal of the solvent. ^{1}H and ^{31}P n.m.r. spectroscopy showed these to be a mixture of [Fe(η^4-C$_5$H$_6$)(dppe)(CO)] (8) and [Fe(η^5-C$_5$H$_5$)(dppe)(CH$_3$)] (9) in the ratio 2 : 3. The i.r. spectrum exhibited a band at $\nu_{max.}$ 2 740 cm^{-1} characteristic of (8).

An identical experiment using LiAlD$_4$ in place of LiAlH$_4$ led to [Fe(η^5-C$_5$H$_5$)(dppe)(CD$_3$)] (11) and [Fe(5-*exo*-η^4-C$_5$H$_5$D)(dppe)(CO)] (10) in the ratio 3 : 2 determined by ^{1}H, ^{2}H, and ^{31}P n.m.r. spectroscopy.

Compound (10) was characterised by comparison of its i.r. and ^{1}H, ^{2}H, and ^{31}P n.m.r. spectra with those of (8) and (16); $\nu_{max.}$ 2 045 cm^{-1} (C–D$_{exo}$); ^{2}H n.m.r. (C$_6$H$_6$) δ 2.75 (D$_{exo}$).

Acknowledgements

We thank the British Petroleum Company Ltd., for a fellowship (to S. J. S.), Laporte-Interox Ltd., for a studentship (to S. E. T.), Dr. A. J. Downs and Mr. A. M. Forster for the Raman spectrum, and Dr. R. T. Aplin for the mass spectra.

References

1 P. Biloen and W. M. H. Sachtler, *Adv. Catal.*, 1981, **30**, 165; R. Eisenberg and D. E. Hendrickson, *ibid.*, 1979, **28**, 79; C. Masters, ' Homogeneous Transition-Metal Catalysis,' Chapman and Hall, London, 1981, pp. 227—239.
2 E. L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479; C. K. Rofer-Depoorter, *ibid.*, 1981, **81**, 447; J. R. Blackborrow, R. J. Daroda, and G. Wilkinson, *Coord. [Chem. Rev.*, 1982, **43**, 17; W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117.
3 W. Tam, G.-Y. Lin, W.-K. Wong, W. A. Kiel, U. K. Wong, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 141.
4 W. Tam, G.-Y. Lin, and J. A. Gladysz, *Organometallics*, 1982, **1**, 525 and refs. therein.
5 J. A. Gladysz, *Adv. Organomet. Chem.*, 1982, **20**, 1.
6 J. R. Sweet and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 2811 and refs. therein.
7 C. P. Casey, M. A. Andrews, D. R. McAlister, W. D. Jones, and S. G. Harsy, *J. Mol. Catal.*, 1981, **13**, 43; C. P. Casey, M. A. Andrews, D. R. McAlister, and J. E. Rinz, *J. Am. Chem. Soc.*, 1980, **102**, 1926.
8 D. L. Thorn, *Organometallics*, 1982, **1**, 197 and refs. therein.
9 K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden, and W. R. Roper, *J. Am. Chem. Soc.*, 1979, **101**, 503.
10 P. A. Kongshang, K. R. Haugen, and R. G. Miller, *J. Am. Chem. Soc.*, 1982, **104**, 627; J. P. Collman and S. R. Winter, *ibid.*, 1973, **95**, 4089.
11 B. B. Wayland and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, 1981, 1709; B. B. Wayland, B. A. Woods, and R. Pierce, *J. Am. Chem. Soc.*, 1982, **104**, 302.
12 P. J. Fagan, K. G. Moloy, and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6959.
13 S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047.
14 P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.
15 T. H. Whitesides and J. Shelley, *J. Organomet. Chem.*, 1975, **92**, 215.
16 C. P. Casey, M. A. Andrews, and J. E. Rinz, *J. Am. Chem. Soc.*, 1979, **101**, 741; W. Tam, W.-K. Wong, and J. A. Gladysz, *ibid.*, 1979, **101**, 1589; J. R. Sweet and W. A. G. Graham, *J. Organomet. Chem.*, 1979, **173**, C9.
17 S. G. Davies, J. Hibberd, S. J. Simpson, and O. Watts, *J. Organomet. Chem.*, 1983, **241**, C31; S. G. Davies and S. J. Simpson, *ibid.*, 1982, **240**, C48; S. G. Davies, J. Hibberd, and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1982, 1404; *J. Organomet. Chem.*, 1983, **246**, C16.
18 S. G. Davies, *J. Organomet. Chem.*, 1979, **179**, C5.
19 G. A. Morris and R. Freeman, *J. Magn. Reson.*, 1978, **29**, 433; G. Bodenhausen, R. Freeman, and G. A. Morris, *ibid.*, 1976, **23**, 171.
20 S. G. Davies, H. Felkin, T. Fillebeen-Khan, F. Tadj, and O. Watts, *J. Chem. Soc., Chem. Commun.*, 1981, 341; S. G. Davies, S. J. Simpson, H. Felkin, F. Tadj, and O. Watts, *J. Chem. Soc., Dalton Trans.*, 1983, 981.
21 H. Felkin, P. J. Knowles, and B. Meunier, *J. Organomet. Chem.*, 1978, **146**, 151.
22 S. G. Davies, S. D. Moon, S. J. Simpson, and S. E. Thomas, *J. Chem. Soc., Dalton Trans.*, 1983, 1805.
23 M. R. Churchill and R. Mason, *Proc. R. Soc. London, Ser. A*, 1964, **279**, 191.
24 R. J. Haines and A. L. DuPreez, *Inorg. Chem.*, 1972, **11**, 330.
25 F. Rasetti, *Phys. Rev.*, 1929, **34**, 367; G. K. Teal and G. E. MacWood, *J. Chem. Phys.*, 1935, **3**, 760; A. G. Davies, E. Lusztyk, J. Lusztyk, U. P. Marti, R. J. H. Clark, and M. J. Stead, *J. Chem. Soc., Perkin Trans. 2*, 1983, 669.
26 G. Consiglio, F. Morandini, and F. Bangerter, *Inorg. Chem.*, 1982, **21**, 455.
27 S. G. Davies, S. J. Simpson, and O. Watts, unpublished work.
28 A. Jungbauer and H. Behrens, *J. Organomet. Chem.*, 1980, **186**, 361.
29 G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 1974, 516; F. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1324.
30 L. Abis, A. Sen, and J. Halpern, *J. Am. Chem. Soc.*, 1978, **100**, 2915.
31 D. F. Shriver, ' The Manipulation of Air-sensitive Compounds,' McGraw-Hill, New York, 1969.
32 R. J. Haines and A. L. DuPreez, *J. Organomet. Chem.*, 1970, **21**, 181.
33 S. J. La Croce, K. P. Menard, and A. R. Cutler, *J. Organomet. Chem.*, 1980, **190**, C79.
34 P. Kalck and R. Poilblanc, *C.R. Acad. Sci., Ser. C*, 1972, **274**, 66.
35 F. L. Dickert and S. W. Hellmann, *Anal. Chem.*, 1980, **52**, 996.

Received 29*th July* 1983; *Paper* 3/1324