Homogeneous Hydrogenation of Buta-1,3-diene and Ethylene Catalysed by Carbonylhydridotris(triphenylphosphine)iridium(I) and by Carbonyltrihydridobis(triphenylphosphine)iridium(III)

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Buta-1,3-diene is catalytically hydrogenated to a mixture of butenes and butane by carbonylhydridotris(triphenylphosphine)iridium(I), $IrH(CO)(PPh_3)_3$, and by carbonyltrihydridobis(triphenylphosphine)iridium(III), $IrH_3(CO)(PPh_3)_2$, at 50° in dimethylformamide. The rates observed could be predicted by the empirical rate equation,

$$-\frac{d[C_4H_6]}{dt} = \frac{(1{\cdot}86 \times 10^{-3} + 0{\cdot}681[PPh_3])[Ir]_0[C_4H_6]}{(1 + 1{\cdot}42 \times 10^4[PPh_3])}$$

where $[Ir]_0 = [IrH(CO)(PPh_3)_3] + [IrH_3(CO)(PPh_3)_2]$.

This equation and additional spectrophotometric and kinetic studies of the individual steps in the catalytic cycle are quantitatively interpreted in terms of a mechanism based on the reductive elimination of butenes by $Ir(\sigma\text{-}C_4H_7)H_2(CO)(PPh_3)_2$ formed from $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ produced by the initial reactions of buta-1,3-diene with both $IrH(CO)(PPh_3)_3$ and $IrH_3(CO)(PPh_3)_2$. The intermediate $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ has been isolated and characterised. Rate data for the hydrogenation of ethylene catalysed by the same system have also been quantitatively interpreted by a fundamentally similar mechanism based on the formation of $Ir(\sigma\text{-}C_2H_5)(CO)(PPh_3)_2$ and its subsequent unimolecular decomposition.

CARBONYLHYDRIDOTRIPHENYLPHOSPHINE complexes of iridium have been used to catalyse the hydrogenation of mono-olefins [1-3] but there has been no previous mechanistic investigation of the hydrogenation of dienes. One possible intermediate in the reaction system, $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$, has already been isolated and characterised by Brown *et al.*[4] from the reaction of buta-1,3-diene (hereafter referred to as ' butadiene '), and $IrH(CO)_2(PPh_3)_2$. We have isolated the same product from the reaction of butadiene and $IrH_3(CO)(PPh_3)_2$ and have established spectroscopically its slower formation from $IrH(CO)(PPh_3)_3$. Although its rate of formation is inhibited by triphenylphosphine, its equilibrium concentration is not much reduced. It reacts rapidly with hydrogen to reform $IrH_3(CO)(PPh_3)_2$ and liberate butene. The results of the catalytic investigation show that the reaction is dramatically inhibited by triphenylphosphine and that the rate also depends on the product of the total iridium and butadiene concentrations. The inhibition of the catalytic rate of ethylene hydrogenation by triphenylphosphine is much less marked but the characteristic dependence of the rate on total iridium and olefin concentration is the same.

The catalyst exists as an equilibrium mixture in the presence of hydrogen and triphenylphosphine,

$$IrH(CO)(PPh_3)_3 + H_2 \rightleftharpoons IrH_3(CO)(PPh_3)_2 + PPh_3 \quad (1)$$

but an interpretation of the inhibition of the hydrogenation of either ethylene or butadiene by hydrogen or phosphine based on this equilibrium alone is entirely unsuccessful. Although the effects of the equilibrium have to be allowed for, the only successful explanation

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[1] L. Vaska, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 89.

[2] M. G. Burnett and R. J. Morrison, *J. Chem. Soc.* (*A*), 1971, 2325.

[3] M. G. Burnett and R. J. Morrison, *J.C.S. Dalton*, 1973, 632.

[4] C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem Soc.* (*A*), 1971, 850.

of the rate laws lies in the kinetic balance of reactions forming and removing low concentrations of the unstable alkyl intermediates.

In both cases, the simplest interpretation requires the bimolecular reaction of the olefin with both $IrH_3(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ and excludes the dissociative reaction *via* $IrH(CO)(PPh_3)_2$. The subsequent mechanism in the case of butadiene differs from that of ethylene because of the stability of $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ compared with $Ir(\sigma\text{-}C_2H_5)(CO)(PPh_3)_2$. The latter complex has been detected[5] by its n.m.r. spectrum during the reaction of $IrH(CO)(PPh_3)_3$ or $IrH(CO)_2(PPh_3)_2$ but only by the use of 10—15 atmospheres of ethylene whereas the former has been isolated and characterised.[4]

EXPERIMENTAL

Reagents.—The complexes $IrH(CO)(PPh_3)_3$ and $IrH_3(CO)(PPh_3)_2$ were prepared as before.[2] Triphenylphosphine, dimethylformamide, and hydrogen were obtained from the same sources and purified as previously described.[2] Butadiene was supplied by I.C.I. Chemicals Ltd. and purified by bulb to bulb distillation. The only detectable impurity in the gas used was about 1% but-1-ene.

The complex $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ was obtained by reacting a solution of $IrH_3(CO)(PPh_3)_2$ in dimethylformamide with butadiene at 50° for 2 h, the product being precipitated from solution by water (the reaction was essentially quantitative) (Found: C, 61·8; H, 4·7. $C_{41}H_{37}IrOP_2$ requires C, 61·6; H, 4·7%; m.p., 140—142°).

Apparatus and Procedure.—The apparatus and procedure used for the catalytic studies have already been described.[2,6] The reaction rates used in the kinetic analysis were always too slow to be affected by the limiting rate of gas solution. The u.v. spectra were recorded with a Perkin-Elmer 402 spectrophotometer using evacuable quartz cells fitted with a subaseal and thermostatted at 50 ± 1°. The cells were initially filled with argon or gaseous reactants and the catalyst solution, prepared in a separate vacuum system, was transferred by a hypodermic syringe. The cell path length, which was normally 1 cm, could be reduced by the use of a quartz block to 0·01 cm when required.

RESULTS

Partition Coefficients.—The partition coefficients of the reactant and product gases in dimethylformamide at 50° are given in Table 1. It should be noticed that the value for hydrogen does not agree with the original determination (0·084). The present value has been confirmed using two different separately calibrated apparatuses and using gas to liquid volume ratios varying from 4 to 0·6. In addition the new value is consistent with the value at 25° (0·041), and at 80° (0·106), in that it gives a linear plot of log(Partition coefficient) *vs.* $1/T$.

TABLE 1

The partition coefficients of reactant and product gases in dimethylformamide at 50°

Compound	H_2	C_4H_6	*cis*-2-C_4H_8	*trans*-2-C_4H_8	1-C_4H_8	C_4H_{10}
Partition coefficient	0·067	21·5	14·7	13·0	12·2	7·0

The Equilibrium of Hydrogen, $IrH(CO)(PPh_3)_3$*, and* $IrH_3(CO)(PPh_3)_2$.—At 50° there is no clear break between the pressure drop due to hydrogen dissolving in the solution and the pressure drop due to its reaction. Consequently the pressure drop due to solution must be calculated and depends entirely on the partition coefficient. Since the partition coefficient was over-estimated, the concentration of hydrogen reacted at equilibrium, calculated from the observed pressure drop, was under-estimated and, consequently, so also was K_1.

Nine additional determinations of K_1 have been made to check the corrected result from the original data[2] (3·65 ± 0·28), and these give a mean value of 4·43 ± 0·30. The mean of all the available data used in the following analysis is K_1 = 4·12 ± 0·22.

The estimate of the rate of reaction (1) at 50° also depends on the equilibrium constant K_1 because of the appreciable back reaction (−1). The combined effect of under-estimating K_1 and over-estimating the partition coefficient is to reduce the calculated forward rate constant k_1. The mechanism of reaction (1) was shown to consist of reactions (2a) and (2b), by experiments at 25°. Although

$$IrH(CO)(PPh_3)_3 \rightleftharpoons IrH(CO)(PPh_3)_2 + PPh_3 \quad (2a)$$

$$IrH(CO)(PPh_3)_2 + H_2 \rightleftharpoons IrH_3(CO)(PPh_3)_2 \quad (2b)$$

that conclusion is unaffected, at 50° the calculated value of $k_{2a}k_{2b}/k_{-2a}$ is revised from 4·88 ± 0·05 to 8·0 ± 1·2 s^{-1} and the agreement between theory and experiment is considerably poorer.

Reactions of Butadiene with $IrH_3(CO)(PPh_3)_2$ *and* $IrH(CO)(PPh_3)_3$.—The i.r. spectrum of the complex isolated from the reaction with $IrH_3(CO)(PPh_3)_2$ contained a band at 1945 cm^{-1}, ν(CO), and the n.m.r. spectrum in deuteriochloroform at room temperature had two sets of broad peaks at τ 6·0 and 8·22. The n.m.r. spectrum was similar to that reported[4] for $Ir(\pi\text{-}1\text{-methylallyl})(CO)(PPh_3)_2$, τ 5·77 and 7·91, but the position of the carbonyl band, measured using a KBr disc, disagreed with that reported[4] in Nujol mull, ν(CO) = 1930 cm^{-1}. The mass spectrum of the compound was also recorded and indicated a molecular weight of 798 (calculated using ^{191}Ir to be 798).

Spectroscopic Reaction Studies.—(a) $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$. The observable u.v. spectrum of 10^{-4}M-$Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ in dimethylformamide at 50° was limited by solvent absorption to wavelengths greater than about 285 nm for 1 cm path length. Above 285 nm, the spectrum * contained one band *ca.* 290 nm, ε *ca.* 10^4 l mol^{-1} cm^{-1}.

The spectrum of a solution held at 50° gradually decreased in intensity over the next 18 h and the peak maximum at 290 nm was gradually replaced by the tail of an intense u.v. peak lying below 290 nm. At the same time, three peaks appeared at 333, 385, and 438 nm. This group of absorption bands closely resembled the u.v. spectrum of $IrCl(CO)(PPh_3)_2$ in intensity and position. The latter spectrum also consists of three bands, $\lambda_{max.}$ 339 nm, ε 3 × 10^3 l mol^{-1} cm^{-1}; $\lambda_{max.}$ 388 nm, ε 4 × 10^3 l mol^{-1} cm^{-1}; and $\lambda_{max.}$ 440 nm, ε 7 × 10^2 l mol^{-1} cm^{-1} (measured at 25°).

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* Electronic spectra and some tabulated experimental data have been deposited in Supplementary Publication No. SUP 21002 (9 pp.). For details of the Supplementary Publication Scheme see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue. (Items less than 10 pp. are sent as full-size copies.)

[5] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc.* (*A*), **1970**, 1392.

[6] D. Bingham and M. G. Burnett, *J. Chem. Soc.* (*A*), 1971, 1782.

(b) $\mathrm{IrH_3(CO)(PPh_3)_2}$ *and butadiene.* The u.v. spectrum of 10^{-4}M-$\mathrm{IrH_3(CO)(PPh_3)_2}$ at wavelengths longer than 285 nm consisted of a continuum of diminishing intensity originating in a strong u.v. band below the wavelength limit of observation. When 0·07M-butadiene was added, a band developed at *ca.* 300 nm so rapidly that it had almost reached its maximum final intensity when the first spectral scan was recorded 20 min after the start of the reaction. The u.v. absorption of butadiene hindered the exact observation of the peak maximum but it approximately corresponded in intensity and position with the u.v. band of $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$. The intensity of the spectrum gradually decreased over the next 18 h and the characteristic triple peaked spectrum of the first experiment appeared.

When the same experiment was repeated with 6×10^{-3}M-$\mathrm{IrH_3(CO)(PPh_3)_2}$ using a path length of 0·01 cm, the first product, $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$, was still formed but over a period of hours rather than minutes and the triple peaked spectrum did not appear even after 18 h.

TABLE 2

The stoicheiometric reaction of butadiene and $\mathrm{IrH_3(CO)(PPh_3)_2}$ in dimethylformamide at 50°

No.	Time/min	$10^4[\mathrm{IrH_3(CO)(PPh_3)_2}]$/M	$10^4[\mathrm{C_4H_6}]$/M	$-10^9d[\mathrm{C_4H_6}]/dt$ / mol l^{-1} s^{-1}		$10^4[\mathrm{C_4H_8}]$/M †		
				obs.	calc. *	1-ene	*trans*-2-ene	*cis*-2-ene
(1)	0	50·5	460	900	432			
	25	35·5	445	308	294			
	50	20·5	430	183	164			
	75	10·5	420	111	82			
	150	Reaction complete				31·6 (63%)	13·9 (28%)	4·8 (9%)
(2)	0	90·2	440	900	738			
	25	63	413	550	484			
	50	42	392	375	306			
	75	28	378	150	197			
	150	Reaction complete				54·4 (61%)	26·5 (29%)	8·8 (10%)
(3)	0	125·6	500	1330	1168			
	25	81·4	456	790	690			
	50	62·2	437	550	506			
	75	46·4	421	425	363			
	150	Reaction complete				77·9 (63%)	30·6 (24%)	15·8 (13%)

* Identical rates are calculated using either equation (4) or (5). † No butane formed in reaction.

(c) $\mathrm{IrH(CO)(PPh_3)_3}$ *and butadiene.* When 10^{-4}M-$\mathrm{IrH(CO)(PPh_3)_3}$ was mixed with 0·07M-butadiene, the single band at 325 nm due to $\mathrm{IrH(CO)(PPh_3)_3}$ was gradually replaced ($t_{\frac{1}{2}} = 25$ min) by a peak below 300 nm with an isosbestic point at 293 nm (ε *ca.* 10^4 l mol^{-1} cm^{-1}). The spectrum diminished in intensity and the triple peaked spectrum again appeared as in the other experiments. The effect of the strong u.v. band associated with the final product, occurred sufficiently early to destroy the isosbestic point and to prevent the observation of the 290 nm band due to $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$. However the position and intensity of the isosbestic point observed early in the experiment was exactly what would be expected if the first product of the reaction were $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$.

When the experiment was repeated in the presence of 3×10^{-3}M-triphenylphosphine, the same spectral changes were observed but the reactions were considerably slower. The amount of $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$ formed was only slightly reduced but the half-life to equilibrium was increased to *ca.* 3 h and the final triple peaked spectrum could only just be distinguished after 15 h.

(d) $\mathrm{IrH_3(CO)(PPh_3)_2}$, *butadiene, and hydrogen.* When 0·045M-butadiene and 0·0016M-hydrogen were mixed with 10^{-4}M-$\mathrm{IrH_3(CO)(PPh_3)_2}$, the spectrum of $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$ did not appear. The continuum due to the combined effects of $\mathrm{IrH_3(CO)(PPh_3)_2}$ and butadiene remained unchanged for *ca.* 1 h and the final triple peaked spectrum developed over the next 18 h. When hydrogen was injected into the gas space of the sealed cell, the spectrum immediately returned to the continuum observed initially. The triple peaked spectrum apparently only appears in the absence of hydrogen. The hydrogen present in the spectroscopic cell is rapidly removed both by the formation of butenes and also by loss to the gas space due to its low solubility in dimethylformamide. The same solution held in the reaction vessel used for catalytic studies, in which there was more hydrogen available, showed a far less intense triple peaked spectrum after 15 h at 50°.

Kinetics of the Reactions.—The quantitative measurements of the rates of these reactions have been made by manometry and gas chromatography in the apparatus used for catalytic studies. The results therefore correspond to the rate of removal of butadiene and formation of butene or butane rather than to the concentration changes of the metal complexes which was the subject of the spectroscopic investigation. The two approaches are therefore complementary.

(a) *Butadiene and* $\mathrm{IrH_3(CO)(PPh_3)_2}$. The results of experiments on the hydrogenation of butadiene by $\mathrm{IrH_3(CO)(PPh_3)_2}$ at 50° in dimethylformamide are given in Table 2. The most striking difference between these experiments and the catalytic experiments described later is the absence of butane in the products. The total amount of butene formed in each case corresponded to the loss of 1 mole of hydrogen from each mole of $\mathrm{IrH_3(CO)(PPh_3)_2}$ present initially. The calculated rates given in column 6 of Table 2 were found from the empirical rate equation derived from the catalytic experiments. The observed rates are generally fairly close to the calculated results. The worst discrepancies occur at the beginning and the end of a reaction where the accuracy of the rate measurements is reduced.

(b) *Butadiene and* $\mathrm{IrH(CO)(PPh_3)_3}$. The reaction of

0·037M-butadiene with 6×10^{-3}M-$IrH(CO)(PPh_3)_3$ was followed manometrically but, due to the large solubility of butadiene, the total expected pressure drop due to reaction was only *ca.* 5 mmHg. The estimated initial rate of reaction (10^{-7}M s^{-1}) is reliable to a factor of 2. The total pressure change occurring over 18 h was only about half that expected for complete reaction. No butenes or butane were formed.

(c) *Hydrogen and* $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$. The complex $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ was found to react very rapidly with hydrogen to reform $IrH_3(CO)(PPh_3)_2$ while liberating a mixture of butenes and butane. The butenes formed were subsequently hydrogenated at a rate normal for the catalysed process although the butane was at first formed so rapidly it could only have come from the direct reaction of the complex and hydrogen. The initial fast uptake of hydrogen calculated from the pressure change and the product analysis was equivalent to 2 moles of hydrogen per mole of complex. The rate of this reaction, calculated from the pressure change in the same way, apparently obeyed equation (3) but it was too fast to allow a reliable

$$-\frac{d[H_2]}{dt} = 22[Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2][H_2] \qquad (3)$$

kinetic study. The product analysis of this experiment (No. 5) is shown in Table 3. In comparing this result with those of the catalytic experiments, allowance must be made for the fact that the product butenes are present in the first few minutes in sufficient concentration for the secondary catalytic processes of isomerisation and reduction to butane to alter the initial product distribution. A blank experiment performed with but-1-ene shows that these processes markedly increase the butane fraction at the expense of but-1-ene (No. 4, Table 3). This explains the high level of butane in experiment 5 after 100 min.

TABLE 3

Hydrogenation and isomerisation of butenes catalysed by $IrH_3(CO)(PPh_3)_2$ in dimethylformamide at 50°

No.	Time/min	$10^4[IrH_3(CO)(PPh_3)_2]$/M	$10^4[H_2]$/M	$10^4[C_4H_8]$/M 1-ene	 *trans*-2-ene	 *cis*-2-ene	$10^4[C_4H_{10}]$/M
(4)	0	75·0	11·8	232	0 (0%)	0 (0%)	0 (0%)
	200	75·0	11·8	155	23·2 (41%)	10·8 (19%)	22·7 (40%)
(5)	5	125·6	12·2	62·9 (50%)	28·2 (23%)	7·9 (6%)	27·0 (21%)
	100	125·6	12·2	30·0 (24%)	34·2 (27%)	9·7 (8%)	51·0 (41%)

But-1-ene is the reactant in No. 4 and $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ in No. 5.

TABLE 4

Rates of hydrogenation of butadiene catalysed by $IrH(CO)(PPh_3)_3$ and $IrH_3(CO)(PPh_3)_2$ in dimethyl formamide at 50°

							-10^9 d[C_4H_6]/d*t* at 200 min mol l^{-1} s^{-1}		
No.	$10^4[Ir]_0$/M	*R* [d]	$10^4[PPh_3]$/M	$10^4[H_2]$/M	$10^4[C_4H_6]$/M	obs.	eqn. (4)	eqn. (5)	eqn. (17)
6 [a]	60·3	0·620	22·9	3·4	230	12·3	14·1	12·4	12·4
7 [a]	64·5	0·629	23·9	3·4	204	13·0	13·1	11·6	11·5
8 [a]	56·6	0·394	34·3	12·8	224	11·7	10·7	10·5	11·5
9 [a]	65·8	0·406	39·1	13·9	221	11·2	11·6	11·7	12·6
10 [a]	61·8	0·385	38·0	14·8	94·6	4·6	4·7	4·7	5·2
11 [a]	66·7	0·466	35·6	9·9	569	30·7	31·5	31·2	32·6
12 [a]	121	0·521	57·9	12·9	235	21·3	19·8	21·4	20·9
13 [b]	62·5	0·402	43·0	15·5	204	9·7	9·8	10·1	10·8
14 [b]	62·0	0·792	236	15·0	220	7·3	7·3	7·3	7·0
15 [c]	73·1	0	0	10·8	245	358	333	333	333
16 [c]	74·6	0	0	13·3	202	223	280	280	280
17 [c]	62·2	0	0	12·2	62·3	87	72	72	72
18 [c]	64·5	0	0	2·4	185	196	222	222	222
19 [c]	64·1	0	0	6·5	198	200	236	236	236
20 [c]	66·5	0	0	11·2	407	423	503	503	503
21 [c]	24·0	0	0	14·2	200	103	89	89	89
22 [c]	147	0	0	14·2	168	563	459	459	459

[a] Nos. 6—12 $IrH(CO)(PPh_3)_3$ used as catalyst. [b] Nos. 13—14 $IrH_3(CO)(PPh_3)_2$ used as catalyst with added triphenylphosphine, initial concentration, $6{\cdot}81 \times 10^{-3}$ M (No. 13); $2{\cdot}85 \times 10^{-1}$M (No. 14). [c] Nos. 15—22 $IrH_3(CO)(PPh_3)_2$ used as catalyst. [d] $R = [IrH(CO)(PPh_3)_3]/[Ir]_0$.

(d) *The hydrogenation of butadiene catalysed by* $IrH(CO)(PPh_3)_3$ *and* $IrH_3(CO)(PPh_3)_2$. The rates of catalysis at 50° in dimethylformamide measured by gas chromatography and pressure change are given in Table 4. No significant variations in product ratio were detected in the course of the slower experiments although, for experiments such as Nos. 20 and 22, hydrogenation and isomerisation of the initially formed butenes began to change the product ratio towards the end of the experiment. The rates of butene or butane formation relative to the corresponding rate of butadiene removal show no systematic variation with conditions. All rates are measured 200 min after the start of the reaction. This time was used since it corresponds to roughly half the total period of observation and is therefore the time at which the most accurate rate measurement can be made. In the slower experiments, the rate is constant during a run but in the faster experiments, in the absence of triphenylphosphine, the reaction rate can decrease. The changes in rate during a run are, however, no more than would be predicted on the basis of the empirical rate equation (4),

$$-\frac{d[C_4H_6]}{dt} = \frac{(1{\cdot}86 \times 10^{-3} + 0{\cdot}681[PPh_3])[Ir]_0[C_4H_6]}{(1 + 1{\cdot}42 \times 10^4[PPh_3])} \quad (4)$$

where $[Ir]_0 = [IrH(CO)(PPh_3)_3] + [IrH_3(CO)(PPh_3)_2]$.

This equation was devised by dividing the data into two blocks depending on whether or not triphenylphosphine was present. In the absence of triphenylphosphine the hydrogen and iridium concentrations were varied by a factor of 7 while in the presence of triphenylphosphine, they were varied by factors of 5 and 2 respectively. The triphenylphosphine concentration was then varied by a factor of 10. Once the effects of changing the concentrations of iridium and butadiene had been allowed for in the way suggested by equation (4), the only factor controlling the rate was the concentration of triphenylphosphine. The variations in reaction rate given by equation (4) can equally well be represented by equation (5). The calculated rates

$$-\frac{d[C_4H_6]}{dt} = \left\{\frac{1{\cdot}78 \times 10^{-3}}{(1 + 5{\cdot}21 \times 10^4[PPh_3])} + \frac{7{\cdot}80 \times 10^{-5}}{(1 + 21[PPh_3])}\right\}[Ir]_0[C_4H_6] \quad (5)$$

given in columns 7 and 8 of Table 4 were obtained from equations (4) and (5) above. The discrepancies show no systematic variation with reaction conditions. The first two pairs of experiments (6 and 7, 8 and 9), were carried out with roughly comparable conditions and their variations from the calculated results are random. The triphenylphosphine concentrations quoted in Table 4 were calculated from the initial conditions using the equilibrium constant K_1.

TABLE 5

Apparent first order rate constants for the formation of $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ in dimethylformamide at 50°, $[C_4H_6] = 0{\cdot}07$M

Number	Method	$[IrH_3(CO)(PPh_3)_2]$/M	$[IrH(CO)(PPh_3)_3]$/M	$[H_2]$/M	$[PPh_3]$/M	$10^4k/s^{-1}$
(1)	Spectroscopic	10^{-4}	0	0	0	>4
(2)	Spectroscopic	0	10^{-4}	0	0	*ca.* 5
(3)	Spectroscopic	0	10^{-4}	0	3×10^{-3}	*ca.* 0·7
(4)	Manometric (initial rate *)	6×10^{-3}	0	0	0	*ca.* 0·3
(5)	Spectroscopic	6×10^{-3}	0	0	0	*ca.* 1
(6)	Gas chromatographic and manometric	6×10^{-3}	0	0	0	1·3
(7)	Gas chromatographic and manometric	0	6×10^{-3}	$10^{-3} - 10^{-4}$	3×10^{-3}	0·06

* The rate is increased by a factor of 2 to allow for the difference between the experimental concentration of butadiene (0·037M) and the standard concentration of 0·07M used in the Table.

DISCUSSION

The stability of the complex $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ has made it possible to study the separate stages in the catalytic hydrogenation. Although the quantitative rate data are restricted to the hydrogenation of butadiene by $IrH_3(CO)(PPh_3)_2$ and to the hydrogenation catalysed by $IrH_3(CO)(PPh_3)_2$–$IrH(CO)(PPh_3)_3$, the associated spectroscopic work has made possible a detailed analysis of the mechanism. In the light of the present experimental work and the associated mechanistic conclusions, it is also now possible to propose a detailed mechanism for the hydrogenation of ethylene catalysed by the same system.

Reactions of Butadiene and $IrH_3(CO)(PPh_3)_2$ *or* $IrH(CO)(PPh_3)_3$.—The reaction of butadiene and $IrH_3(CO)(PPh_3)_2$ gives Ir(π-1-methylallyl)$(CO)(PPh_3)_2$ and butenes but no butane unless hydrogen is present initially. The rate of butadiene removal and butene formation is close to that observed in the catalytic reactions, suggesting that this reaction is an important rate determining factor in the absence of triphenylphosphine. The u.v. and manometric evidence also suggests that the same complex is formed by the reaction of $IrH(CO)(PPh_3)_3$ and butadiene.

The spectroscopic experiments were not designed to produce accurate rate data but they do, at least, give an order of magnitude for the reaction rates. In all the experiments the concentrations of triphenylphosphine, hydrogen, and butadiene are roughly constant during the rate measurements so that, provided allowance is made for any initial concentration differences, the rates of conversion of $IrH_3(CO)(PPh_3)_2$ or $IrH(CO)(PPh_3)_3$ to $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ may be represented by apparent first order rate constants. Estimated values of these constants are summarised in Table 5. Numbers (6) and (7) of Table 5 are actually derived from the catalytic rate equations, either (4) or (5), on the assumption that the rate of $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ formation is the rate determining step for hydrogenation. The fact that estimate number (7) is much smaller than any other in the Table is due to the failure of this assumption. It is obvious from the inhibiting effects of triphenylphosphine that butene or butane formation is only one of a parallel series of reactions of $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ and that much of the complex formed never actually yields butene or butane. Numbers (3)—(5) are derived from experiments in which it seems likely that the measurements are following the formation of $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ directly and in these cases, as well as number (6), $IrH_3(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ seem to react at roughly the same rate, to within a factor of 2. Numbers (1) and (2) are from experiments in which there is very much less triphenylphosphine or hydrogen available than in any other case and in both instances the apparent rate constants are much larger than any other estimate in the Table.

It seems therefore, that under catalytic conditions the initial reaction rate of butadiene with both $IrH_3(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ may well be comparable and that the great differences in catalysed rate are due to later inhibiting processes. The rates of reaction observed spectroscopically at low catalyst concentrations are most reasonably explained by the existence of a fast alternative route removed by triphenylphosphine or hydrogen. It is tempting to suppose that the tendency of the initial rates recorded in Table 2 to be faster than those calculated from the rate equations may be due to this early reaction which is rapidly suppressed later by traces of hydrogen liberated during hydrogenation.

The simplest sequence of rate determining steps suggested by the above argument consists of a triple reaction path involving $\mathrm{IrH_3(CO)(PPh_3)_2}$, $\mathrm{IrH(CO)(PPh_3)_3}$, and the dissociatively formed intermediate $\mathrm{IrH(CO)(PPh_3)_2}$. In the absence of hydrogen, the reaction with $\mathrm{IrH_3(CO)(PPh_3)_2}$ proceeds through (−2b) and (8) but it is rapidly inhibited by (2b) and then replaced by the slower reaction (6). The corresponding reaction with $\mathrm{IrH(CO)(PPh_3)_3}$ occurring through (2a) and (8) is inhibited by triphenylphosphine and then replaced by reaction (7). When the complexes are used as catalysts the fast dissociative path will obviously be unimportant in comparison with reactions (6) and (7).

$$\mathrm{C_4H_6 + IrH_3(CO)(PPh_3)_2 \rightleftharpoons Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2 + H_2} \quad (6)$$

$$\mathrm{C_4H_6 + IrH(CO)(PPh_3)_3 \rightleftharpoons Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2 + PPh_3} \quad (7)$$

$$\mathrm{IrH(CO)(PPh_3)_3 \rightleftharpoons IrH(CO)(PPh_3)_2 + PPh_3} \quad (2a)$$

$$\mathrm{IrH(CO)(PPh_3)_2 + H_2 \rightleftharpoons IrH_3(CO)(PPh_3)_2} \quad (2b)$$

$$\mathrm{C_4H_6 + IrH(CO)(PPh_3)_2 \rightleftharpoons Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2} \quad (8)$$

If the rate were controlled solely by the dissociative process (2a) and (−2b), the apparent first order rate constant for $\mathrm{IrH_3(CO)(PPh_3)_2}$ can be estimated[3] as 2×10^{-3} s^{-1} while that for the reaction with $\mathrm{IrH(CO)(PPh_3)_3}$ is 1 s^{-1}. It seems that the rate observed in the former case is approaching the limit although it is not in the latter. This is consistent with what is known[2] about the greater effect of triphenylphosphine compared with hydrogen in removing $\mathrm{IrH(CO)(PPh_3)_2}$. Current work[7] with these complexes has shown that their reactions can proceed at the limiting rates in the case of dimethyl maleate.

The reactions of $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$ after the rate determining steps naturally do not affect the rates of the butadiene reactions discussed in this section but their probable sequence and character can be inferred from the catalytic studies and the relative rates of product formation.

The discussion of these reactions will be included in the general discussion of the reactions forming the catalytic path.

Reactions of $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$.—The rate of removal of $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$ by hydrogen under typical catalytic concentration conditions is about 10^3 faster than the rate of production of butenes so that it seems likely that the complex can behave as a steady state intermediate. This is confirmed by the fact that its concentration is too small to be detected spectroscopically in the presence of hydrogen. Its mechanism of formation has already been discussed above but the proposed mechanism gives no explanation for the very slow changes finally occurring in the spectrum. The resemblance of the spectrum produced to that of $\mathrm{IrCl(CO)(PPh_3)_2}$ suggests that the product is a similar four-co-ordinate iridium(I) complex. The product is unlikely to be $\mathrm{IrH(CO)(PPh_3)_2}$ since evidence of its formation has been found in the presence of 3×10^{-3}M-triphenylphosphine. Under such conditions, $\mathrm{IrH(CO)(PPh_3)_2}$ would be rapidly and completely converted to $\mathrm{IrH(CO)(PPh_3)_3}$. Furthermore when 2 atoms of hydrogen are removed from $\mathrm{IrH_3(CO)(PPh_3)_2}$ by ethylene, the complex decomposed forming some $\mathrm{IrH(CO)(PPh_3)_3}$ mixed with other unidentified decomposition products.[3] Thus $\mathrm{IrH(CO)(PPh_3)_2}$ is unstable when formed in concentrations of the order of 10^{-3}M.

A possible explanation could lie in the *ortho*-metallation (9), since the product would be expected to react rapidly

$$\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2 \longrightarrow Ir(CO)\{P(C_6H_4)Ph_2\}(PPh_3) + C_4H_8} \quad (9)$$

with hydrogen and is also a four-co-ordinate iridium(I) complex. Fortunately the problem hardly affects the present investigation since the compound is only formed under rather extreme conditions and is certainly not important in the catalytic reactions because of its slow rate of formation.

Catalytic Hydrogenation of Butadiene.—The mechanism of butadiene removal. The evidence discussed up to this point does not suggest any sharp difference in the reactions of $\mathrm{IrH_3(CO)(PPh_3)_2}$ and $\mathrm{IrH(CO)(PPh_3)_3}$ with butadiene and supports the view that they both form a common intermediate $\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2}$ at roughly comparable rates under catalytic conditions. The inhibitory effect of triphenylphosphine must therefore be attributed to its reaction with the intermediate, reforming butadiene rather than to its effect on equilibrium (1) to form a greater proportion of $\mathrm{IrH(CO)(PPh_3)_3}$. The most satisfactory mechanism accounting for the results is given below.

$$\mathrm{IrH_3(CO)(PPh_3)_2 + C_4H_6 \rightleftharpoons Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2 + H_2} \quad (6)$$

$$\mathrm{IrH(CO)(PPh_3)_3 + C_4H_6 \rightleftharpoons Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2 + PPh_3} \quad (7)$$

$$\mathrm{Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2 + H_2 \rightleftharpoons Ir(\sigma\text{-}C_4H_7)H_2(CO)(PPh_3)_2} \quad (10)$$

$$\mathrm{Ir(\sigma\text{-}C_4H_7)H_2(CO)(PPh_3)_2 + PPh_3 \longrightarrow IrH(CO)(PPh_3)_3 + C_4H_8} \quad (11)$$

$$\mathrm{Ir(\sigma\text{-}C_4H_7)H_2(CO)(PPh_3)_2 + PPh_3 \longrightarrow IrH(CO)(PPh_3)_3 + C_4H_6 + H_2} \quad (12)$$

$$\mathrm{Ir(\sigma\text{-}C_4H_7)H_2(CO)(PPh_3)_2 \longrightarrow IrH(CO)(PPh_3)_2 + C_4H_8} \quad (13)$$

$$\mathrm{IrH(CO)(PPh_3)_3 \rightleftharpoons IrH(CO)(PPh_3)_2 + PPh_3} \quad (2a)$$

$$\mathrm{IrH(CO)(PPh_3)_2 + H_2 \rightleftharpoons IrH_3(CO)(PPh_3)_2} \quad (2b)$$

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[7] Unpublished data.

The σ-complex formed in reaction (10) is very likely to be as reactive as the π-complex and we have already shown that the latter is likely to be in a steady state concentration during catalysis. Therefore it is reasonable to analyse the mechanism assuming that both the π and σ intermediates are in the steady state.

$$[\mathrm{Ir}(\pi\text{-}\mathrm{C_4H_7})(\mathrm{CO})(\mathrm{PPh_3})_2] = \frac{\{k_6[\mathrm{IrH_3(CO)(PPh_3)_2}] + k_7[\mathrm{IrH(CO)(PPh_3)_3}]\}[\mathrm{C_4H_6}]}{(k_{-6} + k_{10})[\mathrm{H_2}] + k_{-7}[\mathrm{PPh_3}]} \quad (14)$$

$$[\mathrm{Ir}(\sigma\text{-}\mathrm{C_4H_7})\mathrm{H_2}(\mathrm{CO})(\mathrm{PPh_3})_2] = \frac{k_{10}[\mathrm{Ir}(\pi\text{-}\mathrm{C_4H_7})(\mathrm{CO})(\mathrm{PPh_3})_2][\mathrm{H_2}]}{(k_{11} + k_{12})[\mathrm{PPh_3}] + (k_{-10} + k_{13})} \quad (15)$$

Before using equation (14) it is possible to simplify it by estimating the magnitude of the terms in the denominator. Although we have not measured K_7, it is possible to estimate a lower limit from the fact that in the presence of 3×10^{-3}M-triphenylphosphine and 0·07M-butadiene at least half the initial concentration of $\mathrm{IrH(CO)(PPh_3)_3}$ was finally converted into $\mathrm{Ir}(\pi\text{-}\mathrm{C_4H_7})(\mathrm{CO})(\mathrm{PPh_3})_2$,

i.e. $K_7 > 0{\cdot}1$

Also since $K_1 = K_7/K_6$, $K_6 > 0{\cdot}4$

Under catalytic conditions, spectroscopic, manometric, and chromatographic studies agree that k_6 and k_7 are of similar magnitude and suggest a value of the order of 10^{-3} l mol^{-1} s^{-1}. If this result is combined with the equilibrium constants, then,

$$k_{-6} \sim k_{-7} < 10^{-3}\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

The rate constant for reaction (10) cannot be any less than the rate constant measured experimentally for the liberation of butenes and butane when $\mathrm{Ir}(\pi\text{-}\mathrm{C_4H_7})(\mathrm{CO})(\mathrm{PPh_3})_2$ reacted with hydrogen.

$$k_{10} \geqslant 22\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

$$k_{10} \geqslant 2{\cdot}2 \times 10^4\, k_{-6} \text{ and } 2{\cdot}2 \times 10^4\, k_{-7}$$

It is therefore possible to neglect all terms in the denominator of equation (14) except $k_{10}[\mathrm{H_2}]$. On substituting the simplified form of equation (14) into (15) the steady state concentration of the σ complex is given by equation (16),

$$[\mathrm{Ir}(\sigma\text{-}\mathrm{C_4H_7})\mathrm{H_2}(\mathrm{CO})(\mathrm{PPh_3})_2] = \frac{\{k_6[\mathrm{IrH_3(CO)(PPh_3)_2}] + k_7[\mathrm{IrH(CO)(PPh_3)_3}]\}[\mathrm{C_4H_6}]}{(k_{11} + k_{12})[\mathrm{PPh_3}] + (k_{-10} + k_{13})} \quad (16)$$

The theoretical rate equation is therefore,

$$-\frac{\mathrm{d}[\mathrm{C_4H_6}]}{\mathrm{d}t} = \frac{(k_{11}[\mathrm{PPh_3}] + k_{13})\{k_6[\mathrm{IrH_3(CO)(PPh_3)_2}] + k_7[\mathrm{IrH(CO)(PPh_3)_3}]\}[\mathrm{C_4H_6}]}{(k_{11} + k_{12})[\mathrm{PPh_3}] + (k_{-10} + k_{13})} \quad (17)$$

It is possible to reformulate the mechanism on the assumption that $\mathrm{Ir}(\pi\text{-}\mathrm{C_4H_7})(\mathrm{CO})(\mathrm{PPh_3})_2$ is formed from $\mathrm{Ir}(\sigma\text{-}\mathrm{C_4H_7})\mathrm{H_2}(\mathrm{CO})(\mathrm{PPh_3})_2$ and that the latter is the initial product of reaction (6). The rate equation, derived using the same simplifications employed above, is identical to equation (17). Equation (17) has the same algebraic form as the empirical equation (4) providing $k_6 \sim k_7$ which was the conclusion already reached in the course of studying the individual reactions in the catalytic cycle. The fit of equation (17) to the experimental data is not strongly dependent on the ratio k_6 to k_7. The calculated values in column 9 of Table 4 were found from equation (17) in which $k_6/k_7 = 2$, $k_6k_{11}/(k_{-10} + k_{13}) = 1{\cdot}2$ l^2 mol^{-2} s^{-1}, $k_6k_{13}/(k_{-10} + k_{13}) = 1{\cdot}86 \times 10^{-3}$ l mol^{-1} s^{-1}, and $(k_{11} + k_{12})/(k_{-10} + k_{13}) = 1{\cdot}51 \times 10^4$ l mol^{-1}.

The rate of the stoicheiometric reaction of $\mathrm{IrH_3(CO)(PPh_3)_2}$ and butadiene should not be predicted from equation (17) since in the absence of hydrogen the steady state equations (14) and (15) cannot be set up. However the rates of reaction observed are quite close to those calculated using the empirical rate equations (4) or (5). Reactions (10) and (13) are known to be fast from direct observation so that the reaction (6) must be rate controlling in the stoicheiometric reaction. The hydrogenation catalysed by $\mathrm{IrH_3(CO)(PPh_3)_2}$ in the absence of triphenylphosphine should obey the rate equation,

$$-\frac{\mathrm{d}[\mathrm{C_4H_6}]}{\mathrm{d}t} = \frac{k_{13}k_6[\mathrm{IrH_3(CO)(PPh_3)_2}][\mathrm{C_4H_6}]}{(k_{-10} + k_{13})} \quad (18)$$

In order that the catalysed rate and the stoicheiometric rate of reaction should be the same, $k_{-10} < k_{13}$, in which case $k_6 = 1{\cdot}86 \times 10^{-3}$ l mol^{-1} s^{-1}. The simple dissociative scheme based on reactions (2a), (2b), and (8) giving $\mathrm{Ir}(\pi\text{-}\mathrm{C_4H_7})(\mathrm{CO})(\mathrm{PPh_3})_2$ has already been discussed.

$$\mathrm{IrH(CO)(PPh_3)_3} \rightleftharpoons \mathrm{IrH(CO)(PPh_3)_2} + \mathrm{PPh_3} \quad (2a)$$

$$\mathrm{IrH(CO)(PPh_3)_2} + \mathrm{H_2} \rightleftharpoons \mathrm{IrH_3(CO)(PPh_3)_2} \quad (2b)$$

$$\mathrm{C_4H_6} + \mathrm{IrH(CO)(PPh_3)_2} \rightleftharpoons \mathrm{Ir}(\pi\text{-}\mathrm{C_4H_7})(\mathrm{CO})(\mathrm{PPh_3})_2 \quad (8)$$

Although the scheme is an obvious possibility, the evidence suggests that the fast reaction is rapidly inhibited by hydrogen and triphenylphosphine through (2a) and (2b). The absence of a dissociative path under normal catalytic conditions is supported by the disagreement between the trends predicted by the theoretical equation based on reactions (2a), (2b), (8), and (10)—(13) and those observed in practice. The theoretical rate equation has much in common with equation (17) but it is, in fact, a very poor fit to the rate data. One example of its failure can be appreciated without deriving the equation in detail. In the absence of triphenylphosphine, the concentration of $\mathrm{IrH(CO)(PPh_3)_2}$, and hence also that of the π- and of the σ-complexes, will be decreased by hydrogen through reaction (2b), whereas in the original mechanism all these concentrations were unaffected. Thus the dissociative mechanism must predict that catalysis is inhibited by hydrogen in the absence of triphenylphosphine although there is no hydrogen inhibition term in the empirical equation.

It is quite possible to devise mechanisms suggested by the form of the empirical rate equation (5). The different reaction rates and sensitivity to triphenylphosphine are supposed to be due to two reaction paths based on chemically distinct intermediates but this mechanism requires more assumptions to fit the data than the one proposed. The only arbitrary assumption we have been forced to make is that triphenylphosphine can promote the reductive elimination of butene [reaction (11)]. It is this reaction which transforms the marked inhibition by small concentrations of triphenylphosphine to an almost negligible increase in inhibition at higher concentrations. We have previously pointed out [8] a very similar decrease in the inhibitory power of triphenylphosphine as its concentration increases in the catalysis of hydrogenation by $\text{IrCl(CO)(PPh}_3)_2$.

The Mechanism of Product Formation.—The most striking feature of the rates of product formation is the failure to form butane in the absence of hydrogen (Table 2 compared to Table 4). The fact that the butenes are catalytically hydrogenated in this system (Table 3) is not a satisfactory explanation because the rate of butane formation is not zero at the start of the reaction and it does not significantly increase during an experiment; that is, the product ratios are constant in a particular run. The results imply that the product of the $\text{Ir}(\sigma\text{-C}_4\text{H}_7)\text{H}_2\text{(CO)(PPh}_3)_2$ rearrangement, $\text{Ir}(\sigma\text{-C}_4\text{H}_8)\text{H(CO)(PPh}_3)_2$, does not always simply decompose but can also form $\text{Ir}(\sigma\text{-C}_4\text{H}_9)\text{(CO)(PPh}_3)_2$ and that this complex can, in the presence of hydrogen, form butane. Thus a fraction of the butene formed from the σ-butadienyl complex remains in the complexed state long enough for hydrogen attack to occur leading to butane formation without the intermediate formation of butene. Naturally in the absence of hydrogen these secondary processes do not take place and butane is not formed.

The Catalytic Hydrogenation of Ethylene.—The catalytic hydrogenation of ethylene by $\text{IrH(CO)(PPh}_3)_3$–$\text{IrH}_3\text{(CO)(PPh}_3)_2$ has something in common with the present results particularly in the direct attack of ethylene on both complexes but the differences are equally striking. Other work in progress on the catalytic hydrogenation of dimethyl maleate and fumarate [7] confirms the absence of a general catalytic scheme for all olefinic substrates but it is hardly surprising that some steps are common to all the catalytic cycles.

The error in the partition coefficient for hydrogen does not affect the agreement between the rate equation and the experiments but it does change the constants in the empirical rate equation. The data at 50° in dimethylformamide presented earlier [2,3] have been revised; the results are contained in the Supplementary Publication. Previously we did not set out in detail a mechanism for ethylene hydrogenation because we thought the required equality between k_{19} and k_{20} rather surprising,

$$\text{IrH}_3\text{(CO)(PPh}_3)_2 + \text{C}_2\text{H}_4 \rightleftharpoons \text{Ir}(\sigma\text{-C}_2\text{H}_5)\text{(CO)(PPh}_3)_2 + \text{H}_2 \quad (19)$$

$$\text{IrH(CO)(PPh}_3)_3 + \text{C}_2\text{H}_4 \rightleftharpoons \text{Ir}(\sigma\text{-C}_2\text{H}_5)\text{(CO)(PPh}_3)_2 + \text{PPh}_3 \quad (20)$$

but the present work shows a parallel result. Furthermore the spectroscopic study of $\text{Ir}(\pi\text{-C}_4\text{H}_7)\text{(CO)(PPh}_3)_2$ reveals a slow reaction forming what might be $\overline{\text{Ir(CO)}\{(\text{C}}_6\text{H}_4)\text{PPh}_2\}(\text{PPh}_3)$ and Yagupsky [5] has previously reported that the complex $\text{Ir}(\sigma\text{-C}_2\text{H}_5)\text{(CO)(PPh}_3)_2$ stabilised by 10 atmospheres of ethylene did slowly liberate ethane in the absence of hydrogen. Consequently reaction (21) almost certainly occurs in this

$$\text{Ir}(\sigma\text{-C}_2\text{H}_5)\text{(CO)(PPh}_3)_2 \longrightarrow \overline{\text{Ir(CO)}\{(\text{C}}_6\text{H}_4)\text{PPh}_2\}(\text{PPh}_3) + \text{C}_2\text{H}_6 \quad (21)$$

system and could be the rate determining step. Reaction (22) is apparently plausible as a rate determining

$$\text{Ir}(\sigma\text{-C}_2\text{H}_5)\text{H}_2\text{(CO)(PPh}_3)_2 \longrightarrow \text{IrH(CO)(PPh}_3)_2 + \text{C}_2\text{H}_6 \quad (22)$$

step, but in this system it leads to a hydrogen term in the numerator of the theoretical rate equation which is not observed in the empirical rate equation,

$$-\frac{\text{d}[\text{C}_2\text{H}_4]}{\text{d}t} = \frac{0{\cdot}103[\text{Ir}]_0[\text{C}_2\text{H}_4]}{1 + 1124[\text{H}_2] + 258[\text{PPh}_3]} \quad (23)$$

The theoretical rate equation based on reactions (19)—(21) takes the form,

$$-\frac{\text{d}[\text{C}_2\text{H}_4]}{\text{d}t} = \frac{k_{21}\{k_{19}[\text{IrH}_3\text{(CO)(PPh}_3)_2] + k_{20}[\text{IrH(CO)(PPh}_3)_3]\}[\text{C}_2\text{H}_4]}{k_{21} + k_{19}[\text{H}_2] + k_{-20}[\text{PPh}_3]} \quad (24)$$

Comparing equations (23) and (24) it can be seen that $k_{-19}/k_{-20} = 4{\cdot}36$. Also equations (19) and (20) merely constitute a new route for the establishment of equilibrium (1), so that $K_{20}/K_{19} = K_1$. Since the value of

$$\text{IrH(CO)(PPh}_3)_3 + \text{H}_2 \rightleftharpoons \text{IrH}_3\text{(CO)(PPh}_3)_2 + \text{PPh}_3 \quad (1)$$

K_1 is 4·12, it follows that $k_{19}/k_{20} = 4{\cdot}36/4{\cdot}12 = 1{\cdot}06$. The derived value compares very favourably with the experimental value of one.

An alternative formulation of the mechanism suggested previously,[2] which alters none of the arguments given above, is based on the hypothesis that reactions (19) and (20) form the olefin complex $\text{Ir(C}_2\text{H}_4)\text{H(CO)(PPh}_3)_2$. The rate determining step is then the rearrangement to form $\text{Ir}(\sigma\text{-C}_2\text{H}_5)\text{(CO)(PPh}_3)_2$ prior to faster processes liberating ethane. Work in progress [7] on the catalysed hydrogenation of dimethyl maleate and fumarate and the synthesis of olefin hydrides of the suggested type [9]

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[9] M. S. Fraser and W. H. Baddley, *J. Organometallic Chem.*, 1972, **36**, 377.

show that the mechanism is not impossible but unfortunately there seems no way of deciding the point in a case where the complexes are so unstable.

The General Mechanism of Hydrogenation Catalysed by $IrH_3(CO)(PPh_3)_2$–$IrH(CO)(PPh_3)_3$.—It has become clear in the course of this and parallel work [7] on the hydrogenation of dimethyl maleate that, although a general set of possible reactions can be listed, the particular substrate determines which reactions are dominant and the final mechanistic and kinetic picture can vary widely. The marked differences in the catalysed rate and rate equations for ethylene and butadiene originate in the greater stability of $Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ compared with $Ir(\sigma\text{-}C_2H_5)(CO)(PPh_3)_2$.

Perhaps the least expected aspect of this work is the failure of the conventional mechanism of catalysis which usually depends on an interlocked series of equilibria [10] to explain inhibition effects. Furthermore although no kinetic intermediate is postulated which fails to contain either 16 or 18 valence electrons, the transition states of many of the elementary steps [reactions (6), (7), (11), (12), (19), and (20)] can be written as 20 electron systems and they must therefore violate Tolman's rules.[11]

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