The Kinetics of the Reaction of $[Ru(Cl)H(PPh_3)_3]$ with Various Olefins

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A detailed kinetic investigation of the reaction of $[Ru(Cl)H(PPh_3)_3]$ with cycloheptatriene, cyclohepta-1,3-diene, cyclooctatetraene, penta-1,4-diene, cycloocta-1,5-diene and dimethyl maleate, has been carried out spectrophotometrically in CH_2Cl_2 at 10 °C. It is shown that the major mechanism is *via* dissociation of PPh_3 to give $[Ru(Cl)H(PPh_3)_2]$ which then reacts with the olefin. There is also a second mechanism involving direct attack of the olefin on $[Ru(Cl)H(PPh_3)_3]$.

The complex $[Ru(Cl)H(PPh_3)_3]$ is a very valuable hydrogenation catalyst, but its mechanism of action is far from being understood.[1] It is a very difficult system to study due to its great reactivity resulting in such rapid hydrogen consumption that hydrogen starvation can occur in the solution.[2] This is in contrast with $[RhCl(PPh_3)_3]$ which has been thoroughly investigated.[3] In the original paper by Wilkinson and co-workers[4] describing the preparation and initial kinetic investigations of the catalytic activity of $[Ru(Cl)H(PPh_3)_3]$, it was tentatively concluded that the active species is $[Ru(Cl)H(PPh_3)_2]$, but this was, in part, by analogy with the $[RhH(CO)(PPh_3)_3]$ system and by showing inhibition by PPh_3.[4] Support for this suggestion came from the isolation of $[Ru(Cl)H(PPh_3)_2]$ by treating $[\overline{Ru(C_6H_4P}Ph_2)(PPh_3)Cl]$ with hydrogen[5] and $[RuBr_3(PPh_3)_2]$ reacts with H_2 to give $[Ru(Br)H(PPh_3)_2]$.[6] More recently, it has been established that $[Ru(Cl)H(PPh_3)_3]$ undergoes dissociative PPh_3 exchange.[7] The complex $[\{Ru(Cl)H(PPh_3)_2\}_2]$ is an effective hydrogenation catalyst in dimethylacetamide, and the kinetics for its action as a hydrogenation catalyst for acrylamide were determined.[8] The mechanism involves a $[Ru(Cl)H(PPh_3)_2]$ species. Hydrogenation catalysed by $[RuCl_2(PPh_3)_3]$ has also been studied.[9] It was found that the mechanism involves first the formation of $[Ru(Cl)H(PPh_3)_3]$ which is the active catalyst. Inhibition by PPh_3 is found and attributed to the formation of $[Ru(Cl)H(PPh_3)_2]$.

The complex $[RuH_4(PPh_3)_3]$ is also a very effective hydrogenation catalyst and its mechanism for the hydrogenation of cyclohexanone has been thoroughly investigated.[10] The mechanism was shown to involve the initial loss of H_2 to give $[RuH_2(PPh_3)_3]$, which rapidly co-ordinates the cyclohexanone to give $[RuH_2(PPh_3)_3(C_6H_{10}O)]$. This complex reacts with H_2 to give $[RuH_2(PPh_3)_3(C_6H_{11}OH)]$, and finally the cyclohexanol is displaced by H_2, to give $[RuH_4(PPh_3)_3]$ and cyclohexanol. Although $[Ru(Cl)H(PPh_3)_3]$ could, in the presence of H_2, yield $[RuH_4(PPh_3)_3]$ which would then be the catalyst, this is unlikely, and there is no evidence for this reaction. It is more probable that the hydrogenation catalysis by $[Ru(Cl)H(PPh_3)_3]$ involves species which still have chloride co-ordinated to the ruthenium.

Results and Discussion

The Kinetics of the Reaction of $[Ru(Cl)H(PPh_3)_3]$ *and Cycloheptatriene.*—Previous work had shown that the reaction of $[Ru(Cl)H(PPh_3)_3]$ with cycloheptatriene proceeds smoothly to give $[Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2]$.[11a] The reaction is easy to follow by electronic spectroscopy as the starting material, $[Ru(Cl)H(PPh_3)_3]$, is purple, and the product, $[Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2]$, is yellow-brown. The reaction proceeds at a convenient rate at 10 °C, and was therefore studied at this temperature. The reaction was always carried out with at least a ten-fold excess of cycloheptatriene over $[Ru(Cl)H(PPh_3)_3]$, so that pseudo-first-order kinetics could be used. Triphenylphosphine is liberated during the reaction, but is at very low concentration, as the concentration of $[Ru(Cl)H(PPh_3)_3]$ is only *ca.* 10^{-5} mol dm^{-3}. Examination of the PPh_3 dependence of the rate constant shows that at this concentration the effect on the rate constant is negligible, see below. The rate constants obtained spectrophotometrically for various concentrations of cycloheptatriene and PPh_3 are collected in Table 1.

Examination of the data in Table 1 shows that the reaction rate is enhanced linearly, but only slightly by the addition of cycloheptatriene, and there is a non-zero intercept, see Fig. 1. The reaction rate is inhibited by the addition of PPh_3, see Fig. 2.

These data are consistent with the mechanism given in Scheme 1. It is necessary to propose two different ways for the reaction to proceed. The dominant mechanism is the initial loss of PPh_3 to give $[Ru(Cl)H(PPh_3)_2]$, which then can either react with PPh_3 to give $[Ru(Cl)H(PPh_3)_3]$ or with cycloheptatriene to give $[Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2]$. The pre-dissociation of PPh_3 has been suggested previously[4] and then proven by magnetization transfer measurements.[7] The rate of this mechanism is set by the rate of PPh_3 dissociation to give $[Ru(Cl)H(PPh_3)_2]$, and is independent of the concentration of C_7H_8, but is slowed by the addition of PPh_3. The second slower mechanism is the direct attack of cycloheptatriene on $[Ru(Cl)H(PPh_3)_3]$ to give

Table 1 Rate constants for the reaction of $[Ru(Cl)H(PPh_3)_3]$ with cycloheptatriene in CH_2Cl_2 at 283.2 K

$[C_7H_8]$/mol dm^{-3}	$[PPh_3]$/mol dm^{-3}	10^4k_{obs}/s^{-1}
0.0289	0.0	4.09
0.0482	0.0	4.15
0.0964	0.0	4.38
0.241	0.0	4.79
0.578	0.0	5.60
0.771	0.0	6.06
0.0482	0.003	3.40
0.0482	0.01	2.68
0.0482	0.02	1.92
0.0482	0.035	1.58
0.0482	0.05	1.30
0.0482	0.075	1.05
0.241	0.01	4.22
0.241	0.05	3.03
0.241	0.10	2.31

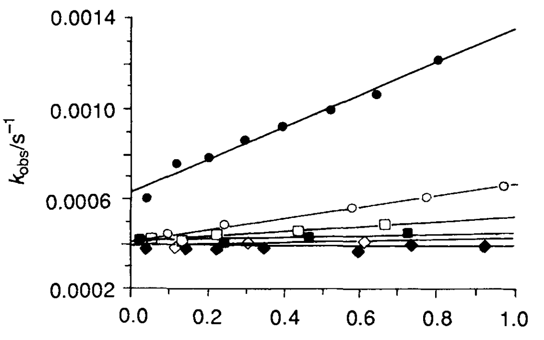


Fig. 1 A plot of the rate of the reaction of $[Ru(Cl)H(PPh_3)_3]$ with various olefins, as a function of C_7H_8 concentration, in the absence of added PPh_3 in CH_2Cl_2 at 283.2 K; cyclohepta-1,3-diene (◆), cycloocta-1,5-diene (◇), penta-1,4-diene (■), cyclooctatetraene (□), cycloheptatriene (○), dimethyl maleate (●)

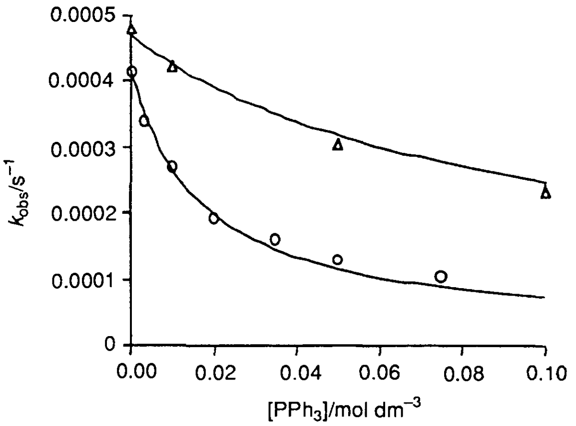


Fig. 2 A plot of the rate of the reaction of $[Ru(Cl)H(PPh_3)_3]$ with C_7H_8, as a function of PPh_3 concentration in CH_2Cl_2 at 283.2 K; $[C_7H_8]$ = 0.0482 (○) or 0.241 mol dm^{-3} (△). The fitted lines were calculated using equation (1) with $k_1 = 4.05\ (\pm 0.06) \times 10^{-4}$ s^{-1}, $k_{-1}/k_3 = 2.9\ (\pm 0.2)$, $k_2 = 2.61\ (\pm 0.16) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}

$[Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2]$ and depends on the concentration of C_7H_8.

Analysis of the mechanism in Scheme 1 gives the rate law given in equation (1).

$$k_{obs} = \frac{k_1[C_7H_8]}{(k_{-1}/k_3)[PPh_3] + [C_7H_8]} + k_2[C_7H_8] \qquad (1)$$

Without PPh_3 added to the solution, the term $(k_{-1}/k_3)[PPh_3]$ can be approximated to zero and the rate-law is reduced to equation (2) as illustrated in Fig. 1. In the presence of PPh_3, all

$$k_{obs} = k_1 + k_2[C_7H_8] \qquad (2)$$

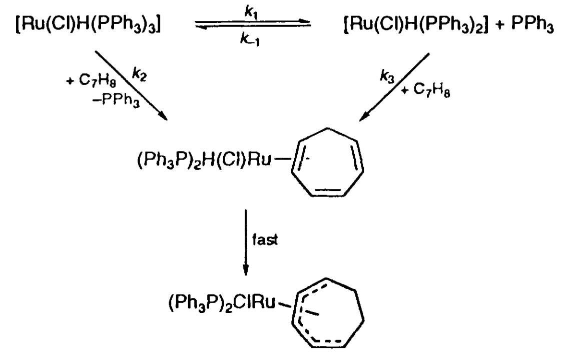
terms operate. The values of k_{obs}, $[PPh_3]$, and $[C_7H_8]$ were fitted to equation (1) using a non-linear, least-squares curve fitting program, and a good fit was obtained yielding the kinetic constants: $k_1 = 4.05\ (\pm 0.06) \times 10^{-4}$ s^{-1}, $k_{-1}/k_3 = 2.9\ (\pm 0.2)$, $k_2 = 2.61\ (\pm 0.16) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, see Fig. 2.

In the absence of added PPh_3, the concentration of liberated PPh_3 is negligible, and equation (2) applies. Using this analysis, the rates in Table 2 were obtained, which for cycloheptatriene are not significantly different from those obtained using the full equation (1).

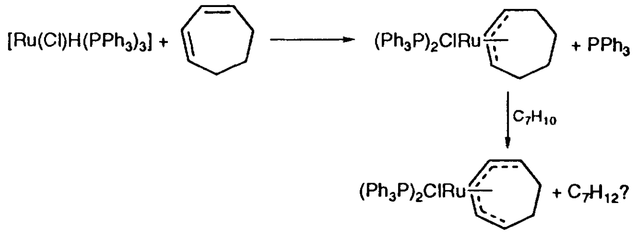
A further check on the validity of this mechanism comes from repeating the measurements with other dienes and trienes. It is predicted that k_1 should be independent of the olefin chosen.

Table 2 The values for k_1 and k_2 derived using equation (2) for a variety of olefins [C_7H_8 = cycloheptatriene, C_7H_{10} = cyclohepta-1,3-diene, C_8H_8 = cyclooctatetraene, 1,4-C_5H_8 = penta-1,4-diene, 1,5-C_8H_{12} = cycloocta-1,5-diene, $C_2H_2(CO_2Me)_2$ = dimethyl maleate]

Olefin	$10^4k_1/s^{-1}$	$10^4k_2/s^{-1}$
C_7H_8	4.08	2.61
C_7H_{10}	3.91	0.00
$C_2H_2(CO_2Me)_2$	6.20	7.38
1,5-C_8H_{12}	3.85	0.30
1,4-C_5H_8	4.14	0.31
C_8H_8	4.07	1.03



Scheme 1 The proposed mechanism for the reaction of $[Ru(Cl)H(PPh_3)_3]$ with cycloheptatriene



Scheme 2 The reaction of $[Ru(Cl)H(PPh_3)_3]$ with cyclohepta-1,3-diene

The Kinetics of the Reaction of $[Ru(Cl)H(PPh_3)_3]$ *and Cyclohepta-*1,3-*diene*.—Previous work has shown that this is not a single reaction, but consists of two steps.[11a] The initial reaction gives the expected product, $[Ru(\eta^3\text{-}C_7H_9)Cl(PPh_3)_2]$, but there is then a hydrogen-transfer reaction between free cyclohepta-1,3-diene and $[Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2]$ to yield $[Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2]$ and presumably cycloheptene, see Scheme 2.*

The second reaction proceeds at a rate comparable with the first, which made the full analysis of the rate data from electronic spectroscopy subject to error. However reasonable rates could be obtained from the initial gradient, see Tables 2 and 3.

The Kinetics of the Reaction of $[Ru(Cl)H(PPh_3)_3]$ *and Cyclooctatetraene*.—The reaction between $[Ru(Cl)H(PPh_3)_3]$ and cyclooctatetraene has been shown to yield a mixture of three products, see Scheme 3.[12]

The reaction proceeds cleanly as a single step reaction, yielding the rate data in Table 2.

The Kinetics of the Reaction of $[Ru(Cl)H(PPh_3)_3]$ *and Penta-*1,4-*diene*.—The reaction between $[Ru(Cl)H(PPh_3)_3]$ and penta-1,4-diene has been shown to involve sequential reactions, yielding initially $[Ru(\eta^3\text{-}C_5H_9)Cl(PPh_3)_2]$, then $[Ru(\eta^5\text{-}$

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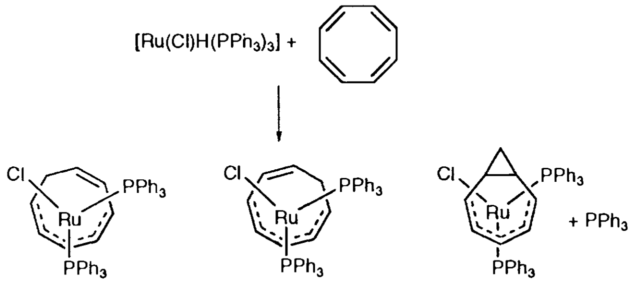
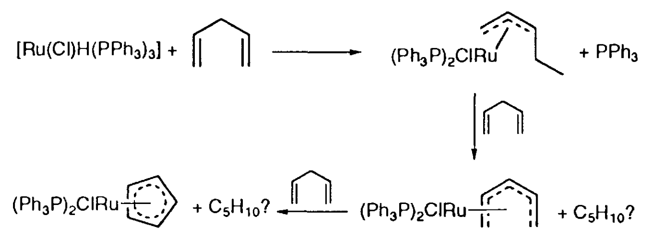
* *Note added at proof:* We now believe that H_2 is liberated. Only traces of cycloheptene are detected and H_2 reverses the reaction.[11b]



Scheme 3 The reaction of $[Ru(Cl)H(PPh_3)_3]$ with cyclooctatetraene



Scheme 4 The reaction of $[Ru(Cl)H(PPh_3)_3]$ with penta-1,4-diene

$C_5H_7)Cl(PPh_3)_2]$ and finally $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$, see Scheme 4.[13,*]

The kinetics of the consumption of $[Ru(Cl)H(PPh_3)_3]$ were determined, see Fig. 1 and Tables 2 and 3.

The Kinetics of the Reaction of $[Ru(Cl)H(PPh_3)_3]$ *and Cycloocta*-1,5-*diene*.—The reaction does not produce olefin insertion into the Ru–H bond, but stops at the diene complex, see Scheme 5.[4,14]

This reaction is analogous to that previously reported between $[Ru(Cl)H(PPh_3)_3]$ and bicyclo[2.2.1]hepta-2,5-diene, which yields **I** as the product.[4,15] In view of the similarity of the kinetics with those observed for the other dienes, cycloheptatriene, and cyclooctatetraene, it is probable that the first stages of the reaction are analogous to those given in Scheme 1, but the reaction stops without insertion of the double bond into the Ru–H bond.

The kinetics of the consumption of $[Ru(Cl)H(PPh_3)_3]$ were determined, see Fig. 1 and Tables 2 and 3.

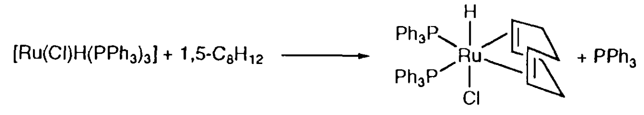
The Kinetics of the Reaction of $[Ru(Cl)H(PPh_3)_3]$ *and Dimethyl Maleate*.—Previous investigations had shown that $[Ru(Cl)H(PPh_3)_3]$ reacts with dimethyl maleate to give $[Ru\{CH(CO_2Me)CH_2CO_2Me\}Cl(PPh_3)_2]$ and PPh_3. Only a single ruthenium containing product was detected by ^1H and ^{31}P NMR spectroscopy, but the stereochemistry was not established.[16]

The kinetics of the consumption of $[Ru(Cl)H(PPh_3)_3]$ were determined, see Fig. 1 and Tables 2 and 3.

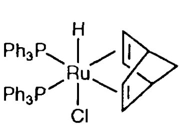
Comparison of the Rate Data.—Previous work has shown the inhibition of the catalytic hydrogenation using $[Ru(Cl)H(PPh_3)_3]$ by PPh_3 and proposed the formation of $[Ru(Cl)H(PPh_3)_2]$ as a key step of the mechanism.[4] The rate data presented here confirm the suggestion that the dissociation of PPh_3 is the rate-determining step. Examination of the rate data in Table 2 shows that k_1 is the same for cycloheptatriene, cyclohepta-1,3-diene, cyclooctatetraene, cyclopenta-1,4-diene and cycloocta-1,5-diene, as is required for the dissociation of PPh_3 from $[Ru(Cl)H(PPh_3)_3]$. Only when dimethyl maleate is used, k_1 is somewhat increased, and this is attributed to a pre-co-ordination of the ester group to the ruthenium before PPh_3 dissociation with a large enough formation constant so that under the reaction conditions, the complex is in effect fully formed. Once $[Ru(Cl)H(PPh_3)_2]$ is formed it has the choice of either reacting with PPh_3 to give back the starting material, and hence the inhibition by PPh_3, or reacting with the olefin to give the product(s).

Table 3 Rate constants for the reaction of $[Ru(Cl)H(PPh_3)_3]$ with various olefins in CH_2Cl_2 at 283.2 K; olefins as in Table 2

Olefin	[Olefin]/ mol dm^{-3}	10^4k_{obs}/s^{-1}
C_7H_{10}	0.046	3.92
	0.138	3.88
	0.230	3.90
	0.346	3.82
	0.461	4.21
	0.599	3.72
	0.737	3.98
	0.922	3.88
C_8H_8	0.0444	4.15
	0.133	4.10
	0.222	4.43
	0.444	4.42
	0.666	4.80
1,4-C_5H_8	0.0483	4.28
	0.242	4.05
	0.725	4.42
1,5-C_8H_{12}	0.122	3.83
	0.305	4.03
	0.610	4.00
$C_2H_2(CO_2Me)_2$	0.0399	5.98
	0.120	7.53
	0.199	7.78
	0.299	8.58
	0.399	9.18
	0.519	9.95
	0.638	10.63
	0.798	12.22



Scheme 5 The reaction of $[Ru(Cl)H(PPh_3)_3]$ with cycloocta-1,5-diene



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There is also a minor direct reaction of the olefin with $[Ru(Cl)H(PPh_3)_3]$. The reaction with the olefin is very dependent on the olefin and presumably depends on the ability of the olefin to co-ordinate to the ruthenium and then to insert into the Ru–H bond. Examination of the data for k_2 in Table 2 shows that the rate decreases in the order dimethyl maleate > cycloheptatriene > cyclooctatetraene > cycloocta-1,5-diene ≈ penta-1,4-diene > cyclohepta-1,3-diene.

The parallel between these observations and the mechanism proven for the hydrogenation of cyclohexene catalysed by $[RhCl(PPh_3)_3]$ is noteworthy.[3] In both cases the major pathway involves fourteen-electron intermediates, namely $[Ru(Cl)H(PPh_3)_2]$ and $[RhCl(PPh_3)_2]$, but a slower pathway also exists involving species containing three PPh_3 ligands.

Experimental

The complex $[Ru(Cl)H(PPh_3)_3]$ was prepared by the literature method.[17] Dichloromethane was freshly distilled over CaH_2.

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[*] *Note added at proof*: We now believe that the formation of $[Ru(\eta^5\text{-}C_5H_7)Cl(PPh_3)_2]$ and $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ involves the loss of H_2.[11b]

The olefins were purchased from Aldrich and passed through alumina and degassed just before use.

The kinetics were followed spectrophotometrically using a Perkin Elmer Lambda 5 spectrophotometer by repetitive scanning in the range 350 to 650 nm. The reactions were carried out in a silica cell sealed with a subaseal in the thermostatted cell compartment with a temperature accuracy of ± 0.05 °C. The use of at least a 10-fold excess of olefin over complex always ensured pseudo-first order conditions. The rate constants were obtained from a non-linear least-squares fit of the experimental A_t, the absorbance at time t, *versus* time data to the expression $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, with A_0, the absorbance at time $t = 0$, A_∞ and k_{obs} as the parameters to be optimized.

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