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The reaction between $[(\eta^5\text{-}C_7H_9)RuCl(H)(PPh_3)_2]$ and dihydrogen [1]

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Abstract

$[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ has been shown to react with hydrogen to give $[(\eta^3\text{-}C_7H_{11})RuCl(PPh_3)_2]$ initially, and then $[RuCl(H)(PPh_3)_3]$, $[Ru_2H_4Cl_2(PPh_3)_4]$, and unidentified compound(s). This is a rare example of the hydrogenation of a coordinated ligand, where the ligand remains coordinated to the metal. It is suggested that the reverse reaction, involving the conversion of $[(\eta^3\text{-}C_7H_{11})RuCl(PPh_3)_2]$ to $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ is a rare example of the loss of dihydrogen from a coordinated ligand. © 1998 Elsevier Science S.A.

Keywords: $[(\eta^5\text{-}C_7H_9)RuCl(H)(PPh_3)_2]$; Dihydrogen; Ligand

It has been previously shown that $[RuCl(H)(PPh_3)_3]$ reacts with cyclohepta-1,3-diene to give initially $[(\eta^3\text{-}C_7H_{11})RuCl(PPh_3)_2]$ and then $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ [1]. Similarly, $[RuCl(H)(PPh_3)_3]$ reacts with penta-1,4-diene to give initially $[(\eta^3\text{-}C_5H_9)RuCl(PPh_3)_2]$, then $[(\eta^5\text{-}C_5H_7)RuCl(PPh_3)_2]$ and finally $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ [2]. This was the first observation of the ring closure of a pentadienyl to a cyclopentadienyl, although it had been earlier suggested as occurring in the mass spectrometer [3]. Subsequently, the reaction was exploited to synthesise $[Ru(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)]$ [4], $[Ru(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)_2]$ [4,5], $[Os(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)]$[4], $[Os(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)_2]$ [4], $[Ru(\eta^5\text{-}C_5Me_5)\eta^5\text{-}1,3\text{-}Me_2C_5H_3)]$ [5], $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}1,2\text{-dihydropentalenyl})]$ [5], and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}1,3\text{-}Bu^t_2C_5H_3)]$ [5], albeit under much more forcing conditions. Similar reactions are rare, but when cyclo-octa-1,5-diene reacts with $[Re_2(CO)_{10}]$ at 250°C, (**1**) is formed in a 5% yield [6], and a similar ring closure has been observed on heating (**2**) in the presence of cyclo-octa-1,5-diene to give (**3**) quantitatively (see Scheme 1) [7,8].

The dehydrogenation of a coordinated ligand, which remains coordinated, is uncommon. Examples are the dehydrogenation of the alkane chain of $Ph_2P(CH_2)_6PPh_2$ on reaction with $[(\eta^4\text{-cod})MCl]_2$, M = Rh, Ir, to give [{*trans*-$Ph_2P(CH_2)_2CH{=}CH\text{-}(CH_2)_2PPh_2$}MCl], (**4**) [9], and $[ReH_7\{P(C_6H_4Me\text{-}4)_3\}_2]$ reacts with pentene to give $[Re(\eta^4\text{-}C_5H_8)H_3\{P(C_6H_4Me\text{-}4)_3\}_2]$ [10]. When $[Ni(\eta^4\text{-}1,5\text{-cod})(\eta^6\text{-}1,3,5\text{-}C_8H_{10})]$ is treated with acetylacetone or cyclopentadiene, the cyclooctatriene ligand is lost and the 1,5-cod is converted to a 1,2,5-η^3-C_8H_{13} ligand [11,12].

The first stage of the reaction of $[RuCl(H)(PPh_3)_3]$ is the insertion of the diene into the Ru–H bond to give an allyl, and there are many examples of this process. For example, $[RuH(\eta^4\text{-}1,5\text{-cod})(PMe_2Ph)_3]^+$ reacts with 1,3-dienes to give $[Ru(\eta^3\text{-enyl})Cl(PMe_2Ph)_3]^+$ [13].

There is little information available to suggest a mechanism for the second stage of the reaction. In the original report [1], it was suggested, by analogy with the reaction of $[Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}1,5\text{-cod})]$ with cyclo-octa-1,5-diene [7,8], that the conversion of $[Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2]$ to $[Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2]$ involves the excess of diene acting as a hydrogen acceptor, but no evidence was presented [1]. In this paper, the reaction is examined in greater detail. The initial stages of the reaction have been previously investigated quantitatively and it was shown that there are two reaction pathways [14]. The mechanism which is dominant at low diene concentration involves the loss of PPh_3 to give $[RuCl(H)(PPh_3)_2]$ which then reacts rapidly with the diene to give $[Ru(\eta^3\text{-enyl})Cl(PPh_3)_2]$. A second

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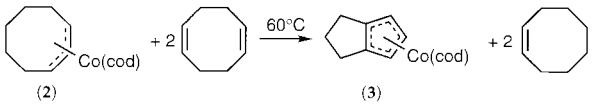
[1] Dedicated to Professor P.M. Maitlis on his 65th birthday.



(2) (3)

Scheme 1. The reaction of [Co(η^3-C_8H_{13})(η^4-1,5-cod)] with cycloocta-1,5-diene.

mechanism becomes significant at high diene concentration involving the direct attack of the diene on [RuCl(H)(PPh_3)$_3$]. Attempts to extend the kinetic investigation to the subsequent dehydrogenation failed due to irreproducibility of the results [15].

1. Results and discussions

The reaction of [RuCl(H)(PPh_3)$_3$] with cycloheptadiene has been previously examined. It was found that [Ru(η^3-C_7H_{11})Cl(PPh_3)$_2$] is the first product which then goes on to form [Ru(η^5-C_7H_9)Cl(PPh_3)$_2$] [1]. It was suggested that the reduction of the coordinated ligand from (η^3-C_7H_{11}) to (η^5-C_7H_9) was achieved by hydrogen transfer to the excess of cyclohepta-1,3-diene present in solution producing cycloheptene. Attempts to demonstrate the production of cycloheptene failed due to the substantial impurity of cycloheptene in the commercial cyloheptadiene being used in the reaction [1]. The reaction has now been repeated using purer cyclohepta-1,3-diene, which was synthesised from cycloheptene by allylic bromination, the isolation of the 3-bromocycloheptene, and subsequent dehydrobromination to generate cyclohepta-1,3-diene which contained less than 0.3% cycloheptene [16]. When this purer cycloheptadiene was used the amount of cycloheptene formed, as detected using GLC and ^{1}H NMR spectroscopy, was less that 10% of the [Ru(η^5-C_7H_9)Cl(PPh_3)$_2$] formed. Hence, a mechanism involving hydrogen transfer from the coordinated allyl ligand to cyclohepta-1,3-diene to give [Ru(η^5-C_7H_9)Cl(PPh_3)$_2$] and cycloheptene cannot be correct. In order to try to understand the reaction further a number of kinetic investigations were performed at 35°C in CD_2Cl_2 and monitored by ^{1}H NMR spectroscopy. A typical graph of the reaction kinetics is shown in Fig. 1. It has been shown previously that there is a rapid reaction between [RuCl(H)(PPh_3)$_3$] and cycloheptadiene to give initially [Ru(η^3-C_7H_{11})Cl(PPh_3)$_2$]. This initial reaction subsequently slows as it is poisoned by the liberated PPh_3 [14].

Examination of a plot of the ^{1}H NMR signals of [(η^3-C_7H_{11})RuCl(PPh_3)$_2$] at δ 4.05 and δ −7.8 and of the species, [(η^5-C_7H_9)RuCl(PPh_3)$_2$] at δ 5.20 and δ 4.65 against time, shows that the reaction goes fast at first then slows (see Fig. 1). The ^{1}H NMR signals at δ 4.05 and δ −7.8 due to [(η^3-C_7H_{11})RuCl(PPh_3)$_2$] initially increase rapidly during the first few minutes and then very slowly decrease. Over the time, 10 to 560 min, the concentration of [(η^3-C_7H_{11})RuCl(PPh_3)$_2$] is nearly constant, decreasing by only about 25%. The signals at δ 5.20 and δ 4.65 due to [(η^5-C_7H_9)RuCl(PPh_3)$_2$] increase rapidly initially. After approximately 100 min, the rate of formation of [(η^5-C_7H_9)RuCl(PPh_3)$_2$] becomes approximately constant. It would be expected that the rate of formation of [(η^5-C_7H_9)RuCl(PPh_3)$_2$] should be first order in [(η^3-C_7H_{11})RuCl(PPh_3)$_2$] in the presence of a large excess of cyclohepta-1,3-diene if the mechanism involves hydrogen transfer to the cyclohepta-1,3-diene. As the concentration of [(η^3-C_7H_{11})RuCl(PPh_3)$_2$] decreases only very slowly after its initial rapid formation, the slowing in the rate of formation of [(η^5-C_7H_9)RuCl(PPh_3)$_2$] must be due to poisoning. There are two possible poisons, PPh_3 and H_2. PPh_3 is initially liberated when the [RuCl(H)(PPh_3)$_3$] starting material is converted to [(η^3-C_7H_{11})RuCl(PPh_3)$_2$]. However, when PPh_3 is added, there is only a small effect on the rate. Attempts were made to detect liberated hydrogen, but failed. This is attributed to the small quantity of hydrogen produced during a typical reaction.

The effect of hydrogen on the reverse reaction was investigated by passing hydrogen through a solution of [(η^5-C_7H_9)RuCl(PPh_3)$_2$] in CD_2Cl_2 in an NMR tube. When the reaction was carried out below −40°C no reaction was observed. A slow reaction was observed at −6°C. The colour of the solution slowly changed from the yellow of [(η^5-C_7H_9)RuCl(PPh_3)$_2$] to red and subsequently to violet. The reaction was stopped at the red stage by placing the NMR tube into a pre-cooled NMR probe at −80°C. The ^{31}P NMR spectrum showed there were two resonances at δ 65.4 and δ 33.8 with $^2J(^{31}P, ^{31}P) = 33$ Hz. This is due to the formation of the allyl

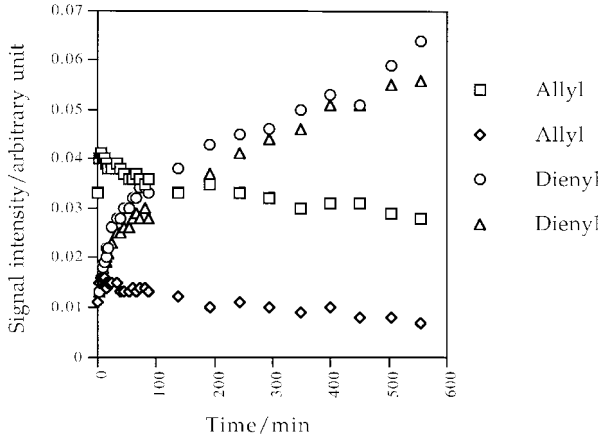


Fig. 1. The plot of intensity of some well-resolved hydrogen NMR signals of [(η^3-C_7H_{11})RuCl(PPh_3)$_2$] and [(η^5-C_7H_9)RuCl(PPh_3)$_2$], monitored by 400 MHz ^{1}H NMR spectroscopy vs. time in CD_2Cl_2 at 35°C. [RuClH(PPh_3)$_3$] (20 mg, 0.022 mmoles), cycloheptadiene (25 μl, 0.23 mmoles); The allyl signals at δ 4.05 (□), δ −7.8 (◇), dienyl signals at δ 5.20 (○), δ 4.65 (△) shown in the figure.

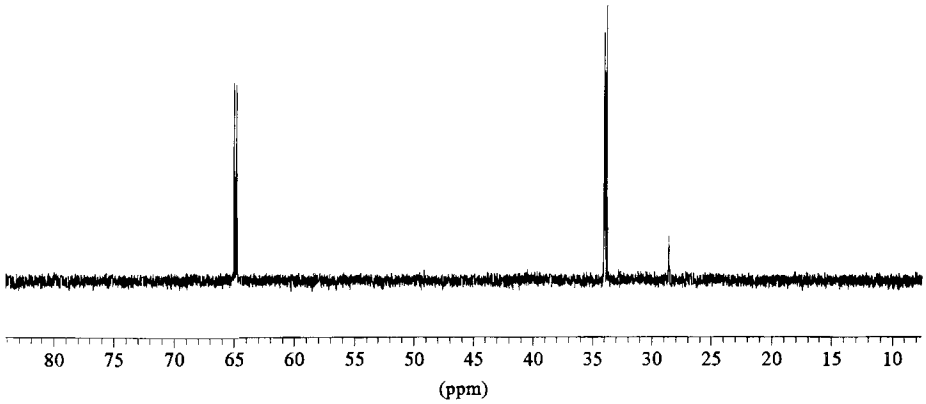


Fig. 2. 162 MHz ^{31}P NMR spectrum at 183 K of $[(\eta^3\text{-}C_7H_{11})RuCl(PPh_3)_2]$ obtained in the reaction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with hydrogen in CD_2Cl_2.

complex, $[(\eta^3\text{-}C_7H_{11})RuCl(PPh_3)_2]$. The species was further confirmed by ^{1}H NMR. A broad signal at δ −7.3 is typical of an agostic hydrogen resonance. The phosphorus and proton chemical shifts are in good agreement with the literature [1]. The ^{31}P NMR spectrum of $[(\eta^3\text{-}C_7H_{11})RuCl(PPh_3)_2]$ is shown in Fig. 2. The signal at δ 28.5 is due to $OPPh_3$.

On further shaking, and gentle warming, the red colour solution turned to purple and all the $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ is hydrogenated to give $[RuCl(H)(PPh_3)_3]$, $[Ru_2H_4Cl_2(PPh_3)_4]$ [17], and an unknown species (see Figs. 3 and 4).

The species, $[RuCl(H)(PPh_3)_3]$, was characterised by ^{31}P NMR, which consists of a triplet at δ 95.0, and a doublet at δ 39.2 with $^2J(^{31}P, ^{31}P) = 29$ Hz. The proton ^{1}H NMR signal at δ −18.52, a quartet at room temperature, is due to the three phosphines becoming equivalent. This is in agreement with the literature [1]. $[Ru_2Cl_2H_4(PPh_3)_4]$ is characterised by comparison of its ^{1}H and ^{31}P NMR data with those published for $[Ru_2Cl_2H_4\{P(tol)_3\}_4]$ [17] (see Table 1).

It can be seen from Table 1 that the proton and phosphorus chemical shifts are similar, but not identical probably due to the differences in the ligand and possibly the concentrations.

The formation of $[RuCl(H)(PPh_3)_3]$ from $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ requires the parallel formation of a ruthenium species with one or no PPh_3 ligands. The NMR spectrum indeed showed that there were some minor species produced. A ^{31}P NMR signal at δ 46.0

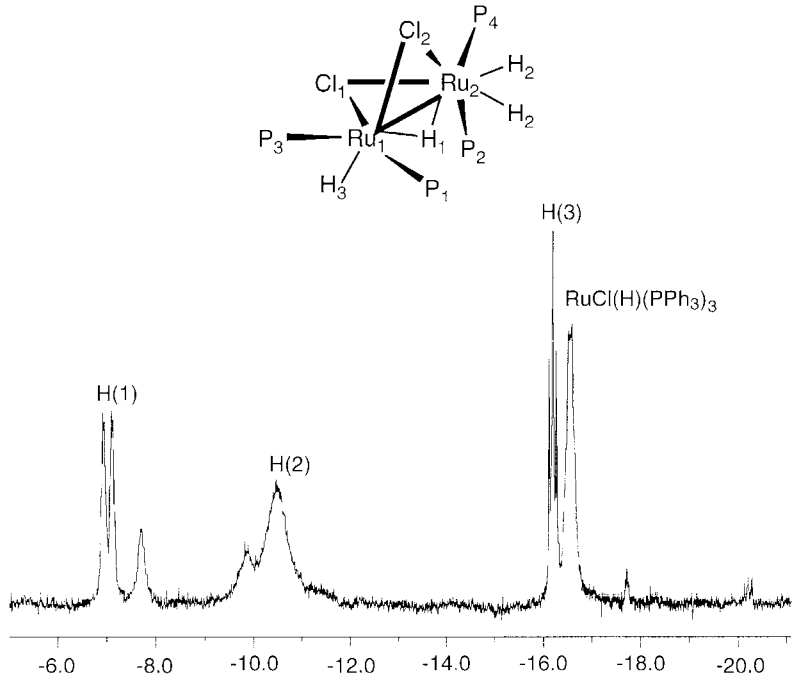


Fig. 3. Partial of ^{1}H 400 MHz NMR Spectrum of $[RuCl(H)(PPh_3)_3]$ and $[Ru_2Cl_2H_4(PPh_3)_4]$ at −90°C. The compounds formed by the reaction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with H_2.

Table 1
Comparison of the ^{1}H and ^{31}P NMR parameters of $[Ru_2Cl_2H_4(PPh_3)_4]$ and $[Ru_2Cl_2H_4\{P(tol)_3\}_4]$

$[Ru_2Cl_2H_4(PPh_3)_4]$ in CD_2Cl_2 at $-90°C$	$[Ru_2Cl_2H_4\{P(C_6H_4Me\text{-}4)_3\}_4]$ in CD_2Cl_2 at $-95°C$
$^{\delta 1}P$ NMR data	$^{\delta 1}P$ NMR data
δ 79.9 {d, $^{2}J(^{31}P, ^{31}P) = 37$ Hz}	δ 74.2 {d, $^{2}J(^{31}P, ^{31}P) = 40$ Hz}
δ 65.0 (d, $^{2}J(^{31}P, ^{31}P) = 17$ Hz)	δ 58.3 (d, $^{2}J(^{31}P, ^{31}P) = 20$ Hz)
δ 62.1 (d, $^{2}J(^{31}P, ^{31}P) = 35$ Hz)	δ 56.3 (dd, $^{2}J(^{31}P, ^{31}P) = 40, 4$ Hz)
δ 36.3 (dd, $^{2}J(^{31}P, ^{31}P) = 37, 17$ Hz)	δ 33.5 (dd, $^{2}J(^{31}P, ^{31}P) = 40, 20$ Hz)
^{1}H NMR data	^{1}H NMR data
δ −7.0 {d, $J(^{31}P, ^{1}H) = 72$ Hz, 1H}	δ −9.2 {d, $J(^{31}P, ^{1}H) = 72$ Hz, 1H}
δ −10.6 (hump, 2H)	δ −11.8 (hump, 2H)
δ −16.4 {t, $J(^{31}P, ^{1}H) = 32$ Hz, 1H}	δ −19.4 {t, $J(^{31}P, ^{1}H) = 28$ Hz, 1H}

and ^{1}H NMR signals at δ −7.7 and δ −9.8 were observed, which could be attributed to the formation of a polyhydride species. Unfortunately, this species was not identified. The organic moiety, $(\eta^5\text{-}C_7H_9)$, was converted into cycloheptene, which gives ^{1}H NMR signals at δ 5.80 (t), δ 2.02 (m), δ 1.65 (m), and δ 1.50 (m) (partially obscured) and cycloheptane which shows a singlet at δ 1.50.

To further investigate the hydrogenation site, D_2 was used. D_2 was generated by using the reaction of sodium metal in freshly distilled THF containing ca. 2% deuterium oxide.

Dideuterium was passed through a solution of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ in CD_2Cl_2 at −6°C. During the period of bubbling, the solution colour changed from light yellow to fresh red in several minutes. The bubbling was stopped and the sample was put into an ethyl acetate slush bath at −84°C to stop the reaction. The ^{31}P NMR spectrum at −40°C showed two sets of doublets of doublets indicating the formation of the allyl intermediates (see Fig. 5).

The expansion ^{31}P NMR spectrum clearly shows two pairs of doublets. The ^{2}H NMR spectrum showed signals at δ −7.8, 1.3 and 2.0. The signal at δ −7.8 is attributed to the agostic deuterium in $[(\eta^3\text{-}C_7H_9D_2)RuCl(PPh_3)_2]$. These observations are consistent with an initial endo addition of the deuterium to $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ followed by a dynamic process where the ruthenium moves its agostic interaction from one side to the other of the cycloheptadienyl ligand (see Scheme 2). It has been previously demonstrated that there is an equilibrium where the ruthenium moves its agostic bonding from one side of the allyl to the other [1].

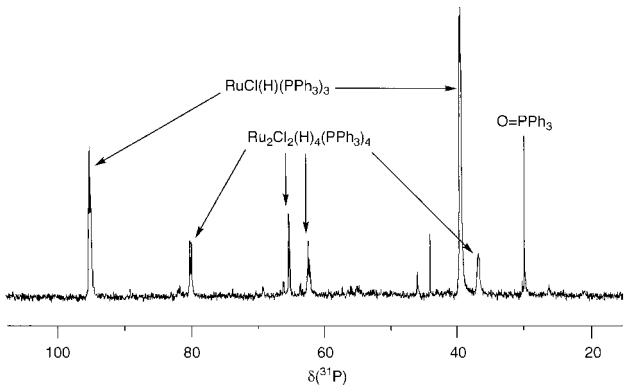


Fig. 4. 162 MHz ^{31}P NMR spectrum of $[RuCl(H)(PPh_3)_3]$ and $[Ru_2Cl_2H_4(PPh_3)_4]$ at −90°C formed by the reaction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with H_2.

In the case of the partially deuterated cycloheptenyl ring, this results in the ruthenium moving between an agostic deuterium and an agostic hydrogen and leads to a mixture of compounds with the ruthenium attached to an agostic deuterium or an agostic hydrogen in approximately equal quantities (see Scheme 2). The signals at δ 64.8 and 33.4, $^{2}J(^{31}P,^{31}P) = 33$ Hz, are tentatively assigned to the species with the agostic deuterium, while the signals at δ 65.2 and 33.6 are assigned to the species with the agostic hydrogen. The difference in chemical shifts is an example of the secondary isotope effect.

The reaction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with H_2 is illustrated in Scheme 3.

The mechanism of the reaction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with dihydrogen is unknown. There are two reasonable mechanisms. It is known that $[(\eta^5\text{-}C_5R_5)RuCl(dippe)]$, R = H, Me, dippe = $Pr^i_2PCH_2CH_2PPr^i_2$, reacts with H_2 to give $[(\eta^5\text{-}C_5R_5)RuH_2(dippe)]^+$ [18]. Alternatively, $[(\eta^5\text{-}C_5Me_5)RuCl(PPr^i_2Ph)]$ reacts with hydrogen to give $[(\eta^5\text{-}C_5Me_5)RuCl(H)_2(PPr^i_2Ph)]$ [19] Hence, it would be reasonable to suggest that dihydrogen reacts with $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ to give either $[(\eta^5\text{-}C_7H_9)\text{-}RuH_2(PPh_3)_2]^+$ or $[(\eta^5\text{-}C_7H_9)RuCl(H_2)(PPh_3)]^+$. [2] There is circumstantial evidence for the latter route. $[(\eta^5\text{-}C_7H_9)RuCl(dppe)]$ was prepared by heating $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with an excess of dppe. Subsequent treatment of $[(\eta^5\text{-}C_7H_9)RuCl(dppe)]$ with dihy-

[2] These compounds could be either dihydrogen or dihydride complexes.

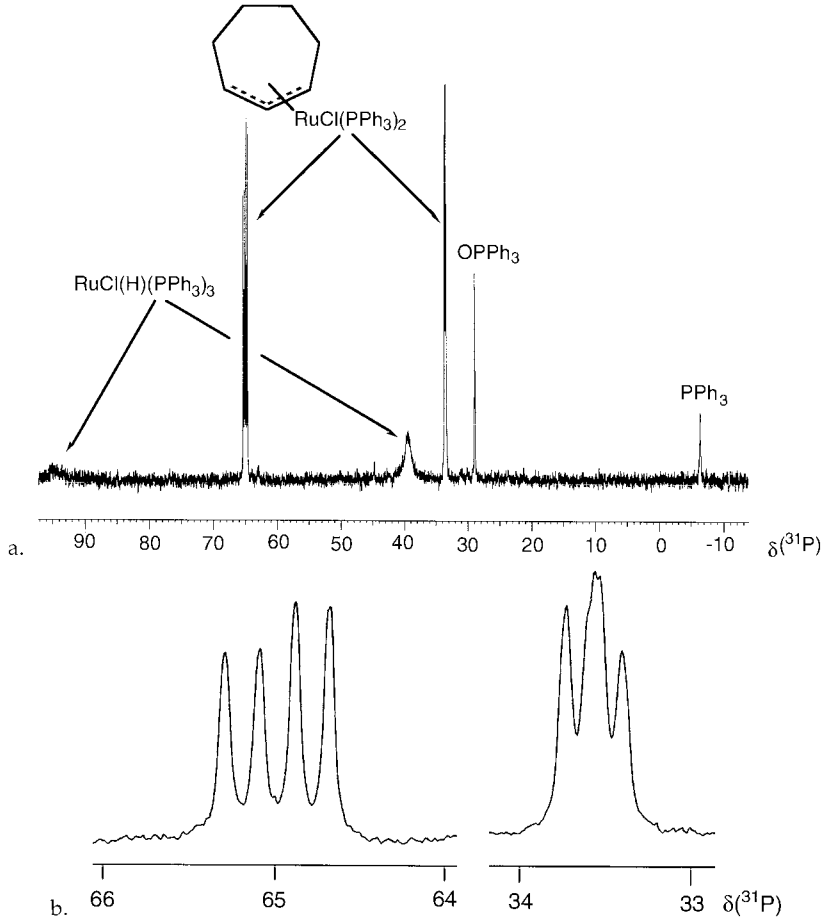
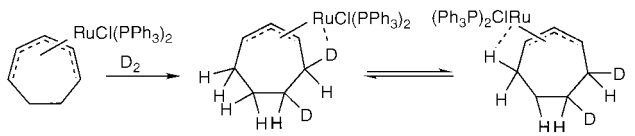
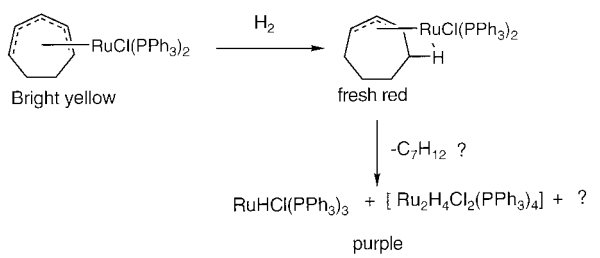


Fig. 5. 162 MHz ^{31}P NMR spectrum of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_{3)2}]$ recorded at −40°C after reaction with D_2 at −6°C. (a) The complete spectrum; (b) the expansion of the signals due to $[(\eta^3\text{-}C_7H_9D_2)RuCl(PPh_3)_2]$).

drogen gave no reaction even after treating for 1 h at 90°C. This observation gives support for the need for PR_3 dissociation prior to reaction with dihydrogen. A determination of the kinetics of PPh_3 displacement from $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ by $P(C_6H_4Me\text{-}4)_3$ and by



Scheme 2. The reaction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with D_2 to give a thermal equilibrium Ru–D–C and Ru–H–C agostic allyl complexes.



Scheme 3. The reaction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ with dihydrogen.

pyridine showed that for $P(C_6H_4Me\text{-}4)_3$ there are two pathways for the reaction, an associative and a dissociative mechanism, while for pyridine, the reaction was exclusively dissociative [20]. In both cases, the reaction proceeded at a steady rate at −29°C.

If the first step of the reaction is the loss of PPh_3 followed by reaction with hydrogen to give $[(\eta^5\text{-}C_7H_9)RuCl(H_2)(PPh_3)]$, [3] then the formation of $[RuCl(H)(PPh_3)_3]$ is readily explained by the reaction of an intermediate such as $[RuCl(H)(PPh_3)_2]$ with the free PPh_3 in solution. As the starting compound contains only two PPh_3 ligands per ruthenium, the formation of $[RuCl(H)(PPh_3)_3]$ requires the formation of a ruthenium species with one or no PPh_3 ligand per ruthenium. There are additional hydride signals observed at δ −7.7 and −9.9 due to an unidentified ruthenium hydride. In addition there are a number of weak ^{31}P NMR signals observed.

The reduction of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ to $[(\eta^3\text{-}C_7H_{11})RuCl(PPh_3)_2]$ is an example of the very rare reduction of a coordinated ligand where the ligand

[3] This compounds could be either a dihydrogen or dihydride complex.

remains coordinated to the metal. This has been observed for $[(\eta^5\text{-}C_5H_5)_2Ni]$, which has been reduced to $[(\eta^3\text{-}C_5H_7)(\eta^5\text{-}C_5H_5)Ni]$ [21]. There have been other examples involving zirconium [22], chromium [23], molybdenum [24], rhenium [25], iron [26] and cobalt [27]. There are numerous examples of ligand reduction resulting in the loss of the ligand. The most relevant example of hydride transfer to a coordinated ligand followed by loss, is the example of $[(\eta^5\text{-}C_5H_5)RuH_2(CO)(PPh_3)]^+$ in acetonitrile where cyclopentadiene is lost and $[RuH(CO)(CNMe)_3(PPh_3)]^+$ is formed [28,29]. A similar reaction is observed when $[(\eta^5\text{-}C_5H_5)Mo(CO)_3H]$ reacts with acetonitrile to give cyclopentadiene and $[Mo(CO)_3(NCMe)_3]$ [30].

2. Experimental

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WH400 spectrometer. The GLC analysis was performed using a Perkin-Elmer 8700 GC with a Chrompak CPSIL5 30 m column.

The syntheses of cycloheptadiene [16] and $[RuCl(H)(PPh_3)_3]$ [31] have been described previously.

2.1. Preparation of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$

$RuCl_3 \cdot nH_2O$ (1.2 g, 0.0048 moles) in dioxan (200 ml) was refluxed for 5 min. After cooling to room temperature, triphenylphosphine (4.8 g, 0.018 moles) was added to the solution. The resulting solution was stirred for two days, and the dark brown solution changed to light green yellow. 1,8-Diazabicyclo[5.4.0]undec-7-ene (2.6 cm^3) was injected into the solution and the solution was refluxed with hydrogen bubbling through it for 1 h, when a violet coloured solution was formed. Degassed cycloheptatriene (1.8 cm^3, 1.58 g, 0.017 moles) was added, and the solution refluxed for 40 min. The solution was then allowed to cool to room temperature. A white grey solid precipitated and was filtered off. The solution was concentrated until fine bright yellow crystals separated. After recrystallisation either from THF or dioxan (20 cm^3), it was filtered and washed with 4 cm^3 of 40–60°C petroleum ether, and dried on the vacuum line. Yield: 3.54 g, 81%. Purity: calc. (%): C, 68.47; H, 5.21; Cl, 4.7; anal: C, 68.05; H, 5.16, Cl, 4.82.

2.2. Preparation of $[(\eta^5\text{-}C_7H_9)RuCl(DPPE)]$ in toluene

A solution of DPPE (107.1 mg) in degassed toluene (10 cm^3) was added to solution of $[(\eta^5\text{-}C_7H_9)RuCl(PPh_3)_2]$ (200 mg, 0.27 mmoles) in toluene (5 cm^3) in a nitrogen filled Schlenk tube. The solution was refluxed for 1 h then was cooled to room temperature, and degassed petroleum ether (b.p. range 45–65°C; 2 cm^3) was slowly added for crystallisation. The yield of the crude product was 0.16 g.

The sample was characterized by ^{31}P NMR spectroscopy, two signals at δ 73.8 and 69.1. The product is quite stable in solution. When exposed to air for two days, the yellow coloured solution slowly changed to dark green.

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