

Preliminary communication

THE PREPARATION OF $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$ FROM $[\text{RuHCl}(\text{PPh}_3)_3]$ AND PENTA-1,4-DIENE; CARBON–CARBON BOND FORMATION BY DEHYDROGENATION

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Summary

$[\text{RuHCl}(\text{PPh}_3)_3]$ reacts with penta-1,4-diene in CD_2Cl_2 , to give initially $[(\eta^3\text{-C}_5\text{H}_9)\text{RuCl}(\text{PPh}_3)_2]$. Dehydrogenation by an excess of pentadiene produces $[(\eta^5\text{-C}_5\text{H}_7)\text{RuCl}(\text{PPh}_3)_2]$. When acetone is used as the dehydrogenating agent, then the reaction proceeds further to yield $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$. This known compound was prepared quantitatively by refluxing $[\text{RuHCl}(\text{PPh}_3)_3]$ and penta-1,4-diene in methyl ethyl ketone.

As part of a study of the reactions of dienes and trienes with $[\text{RuHCl}(\text{PPh}_3)_3]$, we have investigated its reaction with penta-1,4-diene. It had already been established that $[\text{RuHCl}(\text{PPh}_3)_3]$ reacts with cyclohepta-1,3-diene to give initially $[(\eta^3\text{-C}_7\text{H}_{11})\text{RuCl}(\text{PPh}_3)_2]$ which then reacts with an excess of cyclohepta-1,3-diene to give $[(\eta^5\text{-C}_7\text{H}_9)\text{RuCl}(\text{PPh}_3)_2]$ and cycloheptene [1]. It was established that $[(\eta^3\text{-C}_7\text{H}_{11})\text{RuCl}(\text{PPh}_3)_2]$ has a very characteristic ^{31}P NMR spectrum with two doublets at δ 65.3 and 33.7 ppm with $^2J(^{31}\text{P}, ^{31}\text{P})$ 33 Hz.

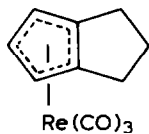
When $[\text{RuHCl}(\text{PPh}_3)_3]$ in CD_2Cl_2 is treated with penta-1,4-diene at -60°C , no reaction occurs, but after warming to room temperature, the ^{31}P NMR spectrum at -60°C shows an AX pattern at δ 67.0 and 31.8 ppm with $^2J(^{31}\text{P}, ^{31}\text{P})$ 33 Hz. It did not prove possible to build up the concentration of this species to a suitable concentration to characterise it further. By comparison of the ^{31}P NMR spectrum with that of the previously characterised $[(\eta^3\text{-C}_7\text{H}_{11})\text{RuCl}(\text{PPh}_3)_2]$, this first species is $(\eta^3\text{-C}_5\text{H}_9)\text{RuCl}(\text{PPh}_3)_2$, but the structure of the allyl is unknown. Attempts to build up the concentration of this species resulted in the formation of a new species with ^{31}P NMR signals at δ 38.0 and 27.4 ppm with $^2J(^{31}\text{P}, ^{31}\text{P})$ 30 Hz. This species was obtained subsequently as ca. 50% of the material present by stirring $[\text{RuHCl}(\text{PPh}_3)_3]$ with penta-1,4-diene in acetone at room temperature for 6 h and then refluxing for 6 h. This material was characterised in solution as $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$.

$C_3H_7RuCl(PPh_3)_2$, (I). At $-40^\circ C$, the 1H NMR spectrum in CD_2Cl_2 (δ in ppm) was fully assigned using decoupling difference NMR spectroscopy. The assignments are H^1 (*anti*) δ -1.57 , $J(H^{1a}, H^2)$ 9 Hz; H^1 (*syn*) δ 0.57 , $J(H^{1s}, H^2)$ 8 Hz; H^2 δ 4.20 , $J(H^2, H^3)$ 6 Hz; H^3 δ 5.74 , $J(H^3, H^4)$ 6 Hz; H^4 δ 5.14 , $J(H^4, H^{5a}) = J(H^4, H^{5s}) = 6$ Hz; H^5 (*anti*) δ -0.32 , H^5 (*syn*) δ 3.06 . At room temperature, rotation of the diene on the $[RuCl(PPh_3)_2]$ moiety, exchanges H^1 and H^5 and H^2 and H^4 , analogous to that previously reported for $[(\eta^5-C_7H_9)Ru(CO)_n\{P(OCH_2)_3-CMe\}_{3-n}]^+$ [2], and $[(\eta^5-C_7H_9)RuCl(PPh_3)_2]$ [1]. This exchange has permitted the confirmation of the 1H NMR signal assignment by magnetisation transfer. The activation energy for rotation is 15 kcal mol $^{-1}$.

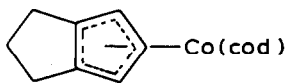
Pure $[(\eta^5-C_5H_7)RuCl(PPh_3)_2]$ could not be synthesised by this route, as attempts to force the completion of the reaction produced a further novel reaction. A new ^{31}P NMR signal appears at δ 38.6 ppm. The formation of this species was carried out by stirring $[RuHCl(PPh_3)_3]$ with penta-1,4-diene for 12 h in methyl ethyl ketone, followed by refluxing for 16 h. ^{31}P NMR spectroscopy showed that the reaction occurs quantitatively to give $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$, which was isolated in 87% yield. The compound was characterised by analysis, mass spectroscopy, and comparison of the 1H and ^{31}P NMR spectra with an authentic sample [3].

The reaction sequence is summarised in Scheme 1. The reaction of penta-1,4-diene with $[RuHCl(PPh_3)_3]$ to give $[(\eta^3-C_5H_9)RuCl(PPh_3)_2]$ is a well established addition of a metal-hydride across a double bond [4]. It is well known that $[RuHCl(PPh_3)_3]$ also catalyses olefin isomerisation. It is therefore assumed that there is subsequent double bond isomerisation to give the allyl product. The concentration of this allyl product is always low. The diene, acetone, or methyl ethyl ketone acts as an oxidising agent, accepting hydrogen from the allyl to generate the dienyl and presumably the diene or ketone is reduced [5].

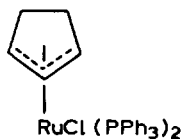
The novel part of the reaction is the following hydrogen transfer to give $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$. Although there are many examples of carbon-carbon



(II)

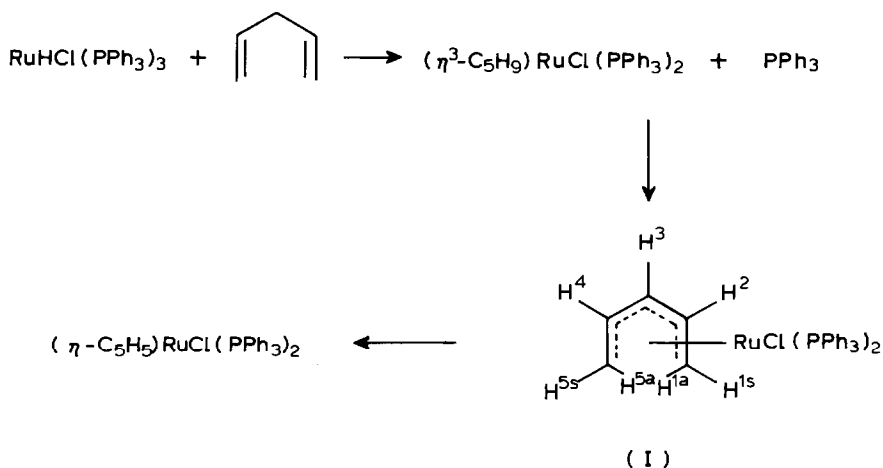


(III)



(IV)

bond formation, mediated by metal complexes, most of the examples involve alkene or alkyne oligomerisation. The formation of carbon-carbon bonds by dehydrogenation is rare in homogeneous systems, although it is common on metal surfaces. One example is that 1,5-cyclooctadiene reacts with $[Re_2(CO)_{10}]$ at $250^\circ C$ to give II, but only in a 5% yield [6]. The mechanism of the reaction is unproven, but probably



SCHEME 1.

follows that proposed for the formation of III, from $\text{Co}(\text{acac})_3$ and cycloocta-1,5-diene [7]. It is therefore proposed that the formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$ goes via $[(\eta^3\text{-C}_5\text{H}_7)\text{RuCl}(\text{PPh}_3)_2]$ (IV). This suggestion is consistent with the observed NMR data on the dienyl complex, I. The ^1H NMR spectrum of $[(\eta^5\text{-C}_5\text{H}_7)\text{RuCl}(\text{PPh}_3)_2]$ shows the *anti* hydrogen atoms at $\delta -0.32$ and -1.57 . This low frequency shift is taken as an indication, but not a proof, that these hydrogen atoms are taking on an 'agostic' character with marked interaction with the metal. This would involve the terminal CH_2 groups twisting out of the plane of the pentadiene to put the *anti*-hydrogen atoms closer to the metal. A further indication of this occurring comes from the approximate equality of the 3J coupling constants to the *syn*- and *anti*-hydrogen atoms. Normally the coupling to the *anti*-hydrogen atom is considerably larger than that to the *syn*-hydrogen atom. The structure of the observed $[(\text{C}_5\text{H}_7)\text{RuCl}(\text{PPh}_3)_2]$ is not IV, as no coupling is observed in the ^1H NMR spectrum between $\text{H}^{1a,s}$ and $\text{H}^{5a,s}$, and such coupling would be observed in IV.

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