

η^3 -Allylruthenium(II) Complexes as Intermediates in Substitution and Isomerization of Diene Ligands; the Dominant Role of Steric Effects

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The formation of $[\text{Ru}(\eta^3\text{-C}_8\text{H}_{13})\text{L}_3]\text{PF}_6$ as intermediates in the conversion of $[\text{RuH}(\text{cod})\text{L}_3]\text{PF}_6$ [cod = cyclo-octa-1,5-diene, L = PMe_3 , $\text{P}(\text{OMe})_2\text{Ph}$, PMe_2Ph , $\text{P}(\text{OMe})\text{Ph}_2$, and $\text{P}(\text{OCH}_2\text{CMe}_3)_3$] into $[\text{RuHL}_4(\text{solvent})]\text{PF}_6$ [L = $\text{P}(\text{OMe})\text{Ph}_2$ and $\text{P}(\text{OCH}_2\text{CMe}_3)_3$] and $[\text{RuHL}_5]\text{PF}_6$ [L = PMe_3 , $\text{P}(\text{OMe})_2\text{Ph}$, and PMe_2Ph] and cyclo-octa-1,3-diene, has been shown to be dependent upon the size of L.

The addition of HBF_4 to a series of iron(0) diene compounds $[\text{Fe}(\eta^4\text{-diene})\{\text{P}(\text{OMe})_3\}_3]$ gives the allyl salts $[\text{Fe}(\eta^3\text{-alkenyl})\{\text{P}(\text{OMe})_3\}_3]\text{BF}_4$. The hydrides $[\text{FeH}(\eta^4\text{-diene})\{\text{P}(\text{OMe})_3\}_3]^+$ were proposed as intermediates in these reactions from deuteration studies, but no spectroscopic evidence was obtained for their presence in solution.¹ In fact no diene-hydride systems have been yet isolated that convert into η^3 -allyl complexes. In our earlier investigations² into the reactivity patterns of the highly labile salt $[\text{RuH}(\text{cod})(\text{NH}_2\text{-NMe}_2)_3]\text{PF}_6$ (**6**) (cod = cyclo-octa-1,5-diene) we isolated complexes $[\text{RuH}(\text{cod})\text{L}_3]\text{PF}_6$ (**1**) with a range of tertiary phosphorus donor ligands L which are analogous to the proposed iron-hydride intermediates. A ^{13}C n.m.r. investigation into the behaviour of (**1**) in solution has now shown the intermediacy of these hydrides in the η^4 -diene \rightarrow η^3 -allyl conversion and the role played by the size of L in this isomerization.

The observed ^{13}C n.m.r. spectra for [**1**; L = PMe_3 , $\text{P}(\text{OMe})_3$, and AsMe_3] at 30 °C in CD_2Cl_2 consisted of four ($2\text{CH}_2 + 2\text{CH}$) C_8 ring resonances with intensities of 1:1:1:1, as expected. Each signal is a second order multiplet owing to coupling with ^{31}P , any carbon being the X-part of an $[\text{AA}'\text{BX}]$ spin system. For the larger ligands L = $\text{P}(\text{OMe})_2\text{Ph}$, PMe_2Ph , $\text{P}(\text{OMe})\text{Ph}_2$, and $\text{P}(\text{OCH}_2\text{CMe}_3)_3$, complex (**1**) at 30 °C in CD_2Cl_2 exhibited five resonances with intensities of 1:2:2:2:1,

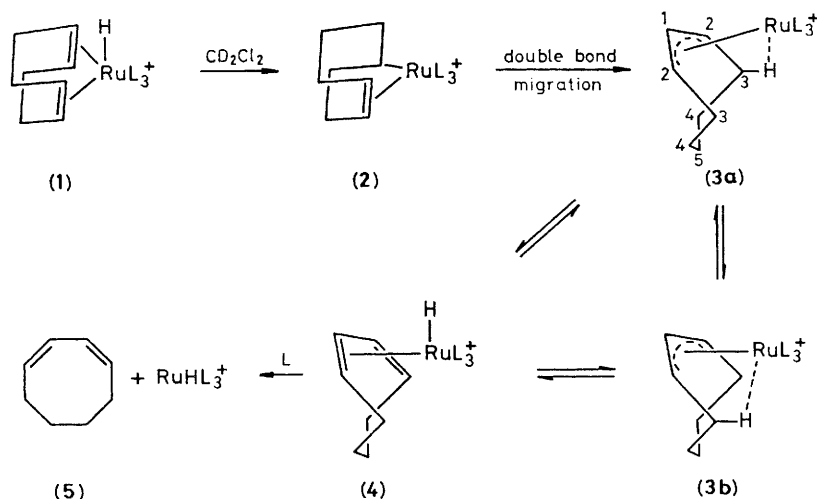
characteristic of the η^3 -cyclo-octenyl complex [**3**; L = $\text{P}(\text{OMe})_2\text{Ph}$, PMe_2Ph , $\text{P}(\text{OMe})\text{Ph}_2$, and $\text{P}(\text{OCH}_2\text{CMe}_3)_3$]. Where multiplicity due to P-C couplings was observed, the signals appeared as binomial quartets suggesting that the phosphorus nuclei are equivalent on the n.m.r. time scale, any carbon being the X-part of an $[\text{A}_3\text{X}]$ spin system. Off-resonance decoupled spectra confirmed the presence of two CH (1:2) and three CH_2 (2:2:1) signals. The two-fold symmetry in the $\eta^3\text{-C}_8\text{H}_{13}$ ring may be caused by a rapid equilibrium between the two equivalent forms (**3a**) and (**3b**) in which the vacant co-ordination site is occupied by the C_3H *endo* proton. In addition, (**4**) could be in slow exchange with (**3a**) and (**3b**) on the route to (**5**). The Ru...HC₃ interaction has been described¹ as a 2-electron 3-centre bond which accounts for the shielding of the proton to -2 p.p.m.

When solutions of [**1**; L = $\text{P}(\text{OMe})_2\text{Ph}$, PMe_2Ph , and $\text{P}(\text{OMe})\text{Ph}_2$] were made up, their ^{13}C n.m.r. spectra run at -20 °C (CD_2Cl_2) showed the four line pattern of the 1,5-diene-hydride. The spectra remained unchanged over a period of days at -20 °C or below, but warming to 30 °C effected a rapid conversion into the five-line η^3 -octenyl spectra of [**3**; L = $\text{P}(\text{OMe})_2\text{Ph}$, PMe_2Ph , and $\text{P}(\text{OMe})\text{Ph}_2$]. Recooling to -40 °C did not reverse the isomerization process. We have not been able to characterize [**1**; L = $\text{P}(\text{OCH}_2\text{CMe}_3)_3$], the isomerization being too rapid even at -60 °C.

Table 1. ^{13}C Chemical shifts for (**1**) and (**3**).

| | PMe_3 | $\text{P}(\text{OMe})_3$ | PMe_2Ph | $\text{P}(\text{OMe})_2\text{Ph}$ | $\text{P}(\text{OMe})\text{Ph}_2$ | AsMe_3 | $\text{P}(\text{OCH}_2\text{CMe}_3)_3$ |
|-------------------------|-------------------|--------------------------|-------------------------|-----------------------------------|-----------------------------------|-----------------|--|
| (1), diene CH | 80.8, 76.1 | 88.8, 85.1 | 81.8, 77.5 | 88.1, 84.6 | 85.8, 81.6 | 73.6, 69.7 | |
| CH ₂ | 32.9, 30.4 | 32.4, 28.6 | 32.1, 28.4 | 32.4, 28.6 | 31.6, 28.6 | 32.3, 29.0 | |
| solvent | a | a | b | b | c | d | |
| (3), allyl C-1 | 98.5 ^f | | 97.0 | 101.1 ^f | 99.1 | | 99.1 |
| C-2 | 64.0 | | 65.9 | 68.9 | 68.8 | | 66.6 |
| C-3, C-4 | 29.5, 28.0 | | 28.7, 29.1 | 28.6, 27.4 | 28.5, 28.5 | | 28.3, 27.2 |
| C-5 | 22.5 | | 21.7 | 21.7 | 21.6 | | 21.7 |
| solvent | d | | a | a | a | | a |

^a CD_2Cl_2 , 30 °C. ^b CD_2Cl_2 , 0 °C. ^c CD_2Cl_2 , -40 °C. ^d $(\text{CD}_3)_2\text{SO}$, 30 °C. ^e CD_3NO_2 , 60 °C. ^f Characterised only in solution. All other compounds were isolated pure in the solid state.



Scheme 1

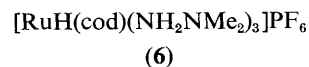
With the smaller ligands, the 1,5-diene hydride was stable at 30 °C and only (**1**; L = PMe_3) converted smoothly above 60 °C in CD_3NO_2 . For (**1**; L = AsMe_3) decomposition occurred above 100 °C in $(\text{CD}_3)_2\text{SO}$ to give cyclo-octa-1,3-diene and a mixture of solvolysed ruthenium hydride complexes of unknown composition.

Cyclo-octa-1,3-diene was readily displaced from [**3**; L = $\text{P}(\text{OMe})_2\text{Ph}$, PMe_2Ph , $\text{P}(\text{OMe})\text{Ph}_2$, and $\text{P}(\text{OCH}_2\text{CMe}_3)_3$] by addition of 1 or 2 mol. equiv. of L in acetone solution to give the solvolysed cation $[\text{RuH}(\text{acetone})\text{L}_4]^+$ [L = $\text{P}(\text{OMe})\text{Ph}_2$ and $\text{P}(\text{OCH}_2\text{CMe}_3)_3$] or $[\text{RuHL}_5]\text{PF}_6$ [**5**; L = $\text{P}(\text{OMe})_2\text{Ph}^3$ and PMe_2Ph^4]. This is in contrast with the $[\text{Fe}(\eta^3\text{-alkenyl})\{\text{P}(\text{OMe})_3\}_3]^+$ systems which only gave $[\text{Fe}(\eta^3\text{-alkenyl})\text{L}\{\text{P}(\text{OMe})_3\}_3]^+$ (L = CO and Bu^tNC) cations.¹ The corresponding hydrides (**5**; L = PMe_3 ,² AsMe_3 , and AsMe_2Ph) were more easily prepared from refluxing solutions of (**3**) in acetone-ethanol with an excess of L. In contrast [**5**; L = $\text{P}(\text{OMe})_3$] cannot be prepared from [**3**; L = $\text{P}(\text{OMe})_3$] and an excess of $\text{P}(\text{OMe})_3$ even under forcing conditions.

A mechanism for these isomerizations is given in Scheme 1. We have investigated the hydride transfer step of this mechanism and have managed to trap the intermediate (**2**) as the complex $[\text{Ru}(1:4\text{-}5\text{-}\eta\text{-C}_8\text{H}_{13})(\text{CNR})_4]\text{PF}_6$ (R = Bu^t and xylyl)⁵ which is not converted into the η^3 -allyl species, indicating the requirement of a free co-ordination site for the isomerization.

The reactivity patterns of (**1**) are being further investigated.

For example (**3**; L = PMe_2Ph) and 1,5-cod react with dihydrogen at room temperature in $(\text{CD}_3)_2\text{CO}$ to give *cis*-cyclo-octene and partially deuterated isopropyl alcohol. The ruthenium-hydrido-species formed in this reaction have not yet been fully characterized.



Further indications of the versatility of (**6**) as a simple route to olefin η^3 -allyl complexes are provided by the formation of $[\text{Ru}(\eta^3\text{-butenyl})(\text{PMe}_2\text{Ph})_3]\text{PF}_6$ from additions of butadiene and PMe_2Ph to (**6**) and the formation of $[\text{Ru}(1\text{-}3:4\text{-}5:6\text{-}7\text{-}\eta\text{-C}_8\text{H}_8)(1,5\text{-cod})]\text{PF}_6$ from cyclo-octatetraene and (**6**).

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