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 $[Ru(\eta^3\text{-}C_8H_{13})L_3]PF_6$ as intermediates in the conversion of $[RuH(cod)L_3]PF_6$ [cod = cyclo-octa-1,5-diene, L = PMe_3, $P(OMe)_2Ph$, PMe_2Ph, $P(OMe)Ph_2$, and $P(OCH_2CMe_3)_3$] into $[RuHL_4(solvent)]PF_6$ [L = $P(OMe)Ph_2$ and $P(OCH_2CMe_3)_3$] and $[RuHL_5]PF_6$ [L = PMe_3, $P(OMe)_2Ph$, 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 $[Fe(\eta^4\text{-diene})\{P(OMe)_3\}_3]$ gives the allyl salts $[Fe(\eta^3\text{-alkenyl})\{P(OMe)_3\}_3]BF_4$. The hydrides $[FeH(\eta^4\text{-diene})\{P(OMe)_3\}_3]^+$ were proposed as intermediates in these reactions from deuteriation 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 investigations[2] into the reactivity patterns of the highly labile salt $[RuH(cod)(NH_2NMe_2)_3]PF_6$ (**6**) (cod = cyclo-octa-1,5-diene) we isolated complexes $[RuH(cod)L_3]PF_6$ (**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.

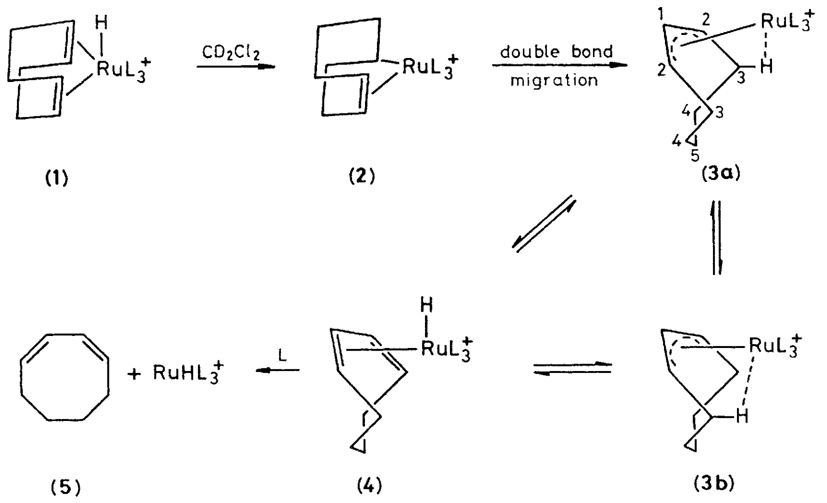
The observed ^{13}C n.m.r. spectra for [**1**; L = PMe_3, $P(OMe)_3$, and $AsMe_3$] at 30 °C in CD_2Cl_2 consisted of four ($2CH_2 + 2CH$) C_8 ring resonances with intensities of 1 : 1 : 1 : 1, as expected. Each signal is a second order multiplet owing to coupling with ^{31}P, any carbon being the X-part of an [AA′BX] spin system. For the larger ligands L = $P(OMe)_2Ph$, PMe_2Ph, $(POMe)Ph_2$, and $P(OCH_2CMe_3)_3$, 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 = $P(OMe)_2Ph$, PMe_2Ph, $P(OMe)Ph_2$, and $P(OCH_2CMe_3)_3$]. 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 $[A_3X]$ 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 $\eta^3\text{-}C_8H_{13}$ 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...HC_3 interaction has been described[1] 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 = $P(OMe)_2Ph$, PMe_2Ph, and $P(OMe)Ph_2$] 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 = $P(OMe)_2Ph$, PMe_2Ph, and $P(OMe)Ph_2$]. Recooling to −40 °C did not reverse the isomerization process. We have not been able to characterize [**1**; L = $P(OCH_2CMe_3)_3$], the isomerization being too rapid even at −60 °C.

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

	PMe_3	$P(OMe)_3$	PMe_2Ph	$P(OMe)_2Ph$	$P(OMe)Ph_2$	$AsMe_3$	$P(OCH_2CMe_3)_3$
(**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] $(CD_3)_2SO$, 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 $(CD_3)_2SO$ 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 = $P(OMe)_2Ph$, PMe_2Ph, $P(OMe)Ph_2$, and $P(OCH_2CMe_3)_3$] by addition of 1 or 2 mol. equiv. of L in acetone solution to give the solvolysed cation $[RuH(acetone)L_4]^+$ [L = $P(OMe)Ph_2$ and $P(OCH_2CMe_3)_3$] or $[RuHL_5]PF_6$ [**5**; L = $P(OMe)_2Ph$[3] and PMe_2Ph[4]]. This is in contrast with the $[Fe(\eta^3\text{-alkenyl})\{P(OMe)_3\}_3]^+$ systems which only gave $[Fe(\eta^3\text{-alkenyl})L\{P(OMe)_3\}_3]^+$ (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 = $P(OMe)_3$] cannot be prepared from [**3**; L = $P(OMe)_3$] and an excess of $P(OMe)_3$ 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 $[Ru(1\!:\!4\text{—}5\text{-}\eta\text{-}C_8H_{13})(CNR)_4]PF_6$ (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 $(CD_3)_2CO$ to give *cis*-cyclo-octene and partially deuteriated isopropyl alcohol. The ruthenium–hydrido-species formed in this reaction have not yet been fully characterized.

$[RuH(cod)(NH_2NMe_2)_3]PF_6$

(**6**)

Further indications of the versatility of (**6**) as a simple route to olefin η^3-allyl complexes are provided by the formation of $[Ru(\eta^3\text{-butenyl})(PMe_2Ph)_3]PF_6$ from additions of butadiene and PMe_2Ph to (**6**) and the formation of $[Ru(1\text{—}3\!:\!4\text{—}5\!:\!6\text{—}7\text{-}\eta\text{-}C_8H_9)(1,5\text{-cod})]PF_6$ from cyclo-octatetraene and (**6**).

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