Journal of Organometallic Chemistry, 276 (1984) C19–C22
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REACTIONS OF HYDRIDO(CYCLOOCTA-1,5-DIENE)TRIS(PHOSPHINE) RUTHENIUM(II) CATIONS WITH 1,3-DIENES: FORMATION OF AGOSTIC η^3-ENYL SPECIES $[Ru(\eta^3\text{-ENYL})L_3]^+$

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(Received July 25th, 1984)

Summary

^{1}H and ^{13}C NMR spectra have shown that the products of the reactions of $[RuH(cycloocta\text{-}1,5\text{-}diene)L_3]^+$ (I, L = PMe_2Ph) with 1,3-dienes are η^3-enyl species and not hydrido(1,3-diene) complexes as inferred previously; similar complexes, with phosphine ligands other than PMe_2Ph, have been prepared.

In an earlier paper [1] we reported the X-ray diffraction study of the product of the reaction of 1,3-butadiene with $[RuH(cod)L_3][PF_6]$ (I) (cod = cycloocta-1,5-diene, L = PMe_2Ph). Our interpretation of the results of the X-ray study led us to assign the hydrido(diene) formulation to this and the cyclohexa-1,3-diene product, although some doubt as to the reliability of the structural results was acknowledged. Our recent work [2] on the formation of η^3-cyclooctenyl species from I (L = a phosphorus donor ligand) prompted us to investigate the solution structures of the products, II, of the 1,3-diene reactions using variable temperature NMR techniques.

Complexes II were obtained by treatment (60°C) of suspensions of I (L = PMe_2Ph, PMe_3, $P(OMe)_2Ph$ and $P(OMe)Ph_2$) in methanol with an excess of the 1,3-dienes (cyclohexa-1,3-diene and cyclohepta-1,3-diene)*. The reaction with 1,3-butadiene was successful only with I (L = PMe_2Ph) as reported previously [1]. The cyclooctadiene was liberated as the 1,3-isomer thus indicating the intermediacy of the η^3-cyclooctenyl complex in the reaction sequence as shown in Scheme 1.

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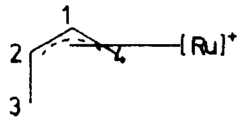
*The products of the reactions were obtained as analytically pure microcrystalline solids, except that the reaction of I (L = PMe_2Ph) with cyclohepta-1,3-diene gave a mixture of IIc and $[Ru(\eta^5\text{-}C_7H_9)(PMe_2Ph)_3][PF_6]$ [6].

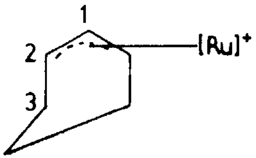
0022-328X/84/$03.00

TABLE 1

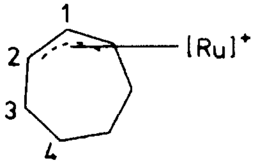
NMR DATA[a] FOR THE COMPLEXES II



(IIa)



(IIb)

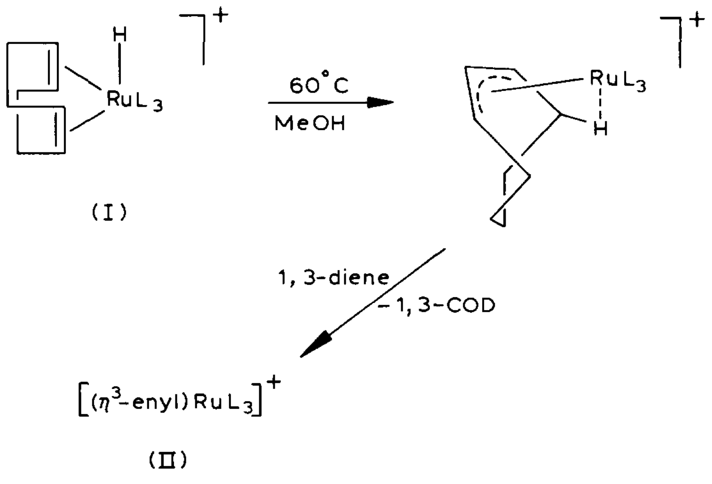


(IIc,IId)

[Ru] ≡ RuL_3; IIa—IIc, L = PMe_2Ph; IId, L = $P(OMe)_2Ph$

Complex	^1H					^{13}C					^{31}P			
	T (K)	H(1)	H(2)	H(3)	H(4)	T (K)	C(1)	C(2)	C(3)	C(4)	T (K)	P	P	J (Hz)
IIa	223	5.25	4.85	−3.85	0.65 *anti*, 2.05 *syn*	253	94.9	67.2	2.8	41.2	293	38.9	−3.2	27
IIb	213	5.05	4.05	1.65 *exo*, −4.25 *endo*	0.75, 0.90	202	90.5	64.9	24.0	17.6	303	34.3	3.5	36
IIc	223	4.80	3.80	1.35 *exo*, −3.85 *endo*	1.00 1.20	223	91.7	62.6	20.6	22.5	Signals obscured by [Ru-(η^5-C_7H_9)(PMe_2Ph)$_3$][PF_6] [6]			
IId	253	4.7	4.0	1.50 *exo* −3.10 *endo*	1.30 1.10	193	96.3	63.5	19.4	22.6	second order			

[a] Values in ppm rel. to TMS (^1H and ^{13}C) and ext. H_3PO_4 (^{31}P).



SCHEME 1

The low temperature NMR spectra of II (L = PMe_2Ph, enyl = butenyl, cyclohexenyl) are given in Table 1 and show that these complexes must be reformulated as η^3-enyl species, in which there is an interaction between the ruthenium ion and the *endo*-CH bond adjacent to the allylic functional group. Thus, the number of ^{13}C signals observed and their s.f.o.r.d.* multiplicities and chemical shifts are consistent [2] only with an allyl functional group. In addition, the high field signals observed in the ^1H NMR spectra of the complexes are characteristic of an agostic [3] $M \cdots H—C$ interaction.

Three fluxional processes could be identified from the variable temperature NMR studies of these complexes; (i) mutual exchange of the phosphorus donor ligands, (ii) a 1,2-metal migration [4] around one face (*endo*) of the carbocyclic ring, and (iii) the exchange [5] of the two *endo*-C_3H hydrogen atoms at the metal. In addition, the butenyl complex exhibited a fourth fluxional process,, methyl group rotation, which was rapid at temperatures as low as 183 K. The exchange of the two *endo*-C_3H hydrogen atoms in the complex II (L = $P(OMe)Ph_2$, enyl = cycloheptenyl) reached the slow exchange limit at 183 K when observed at 500 MHz ($\delta(Ru \cdots H—C) = -8.3$). In contrast, the cyclohexenyl derivative of II (L = $P(OMe)Ph_2$) was still fluxional under these conditions. This result is not consistent with the data for $[Fe(enyl)\{P(OMe)_3\}_3]^+$ complexes, where the barrier to the exchange process increases as the ring size decreases [5].

We are continuing with efforts to obtain spectra of the complexes at temperatures below −100°C. The solid state ^{13}C NMR spectra are consistent with the allyl formulation, and the X-ray determination reported previously must therefore be erroneous. A redetermination of the structure at low temperature is underway.

Acknowledgement. We thank Bruker, West Germany, for the solid state spectra.

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*s.f.o.r.d. = single frequency of resonance decoupled.

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