

Preliminary communication

**HYDROGEN TRANSFER PROCESSES IN THE FORMATION OF
 CATIONIC η^5 -DIENYL COMPLEXES OF RUTHENIUM(II): X-RAY
 STRUCTURE OF $[\text{Ru}(1-5-\eta\text{-CYCLOOCTADIENYL})(\text{PMe}_2\text{Ph})_3][\text{PF}_6]$**

TERENCE V. ASHWORTH, ANTHONY A. CHALMERS, DAVID C. LILES,
 ELSIE MEINTJIES, HESTER E. OOSTHUIZEN and ERIC SINGLETON*

*National Chemical Research Laboratory, Council for Scientific and Industrial Research,
 P.O. Box 395, Pretoria 0001 (Republic of South Africa)*

(Received December 4th, 1984)

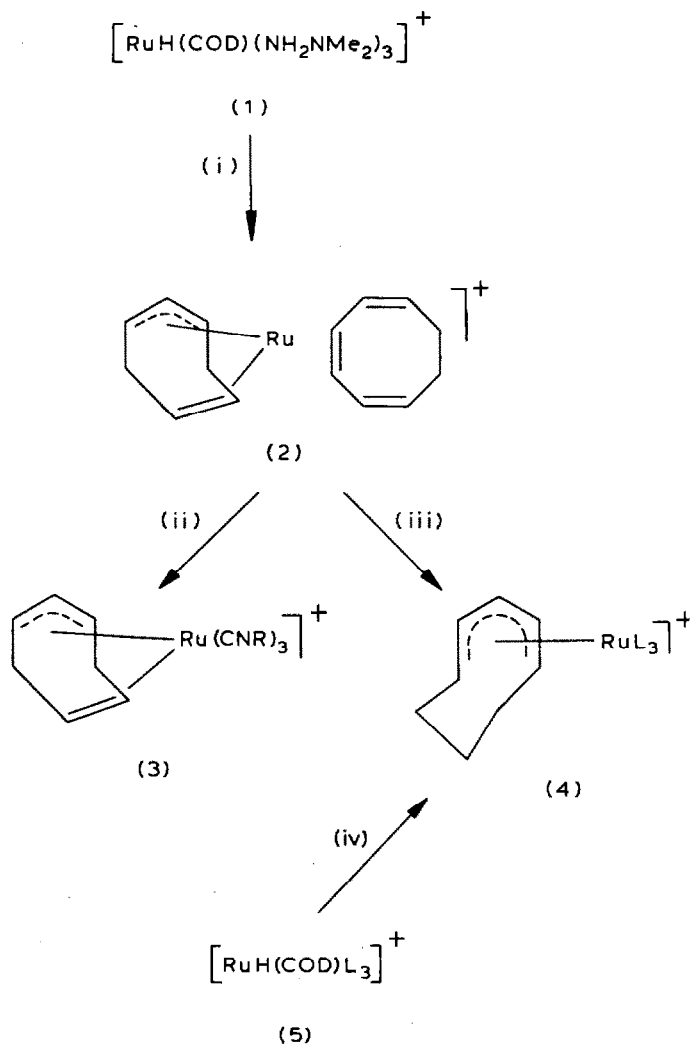
Summary

The cations $[\text{Ru}(1-3:5-6-\eta\text{-C}_8\text{H}_{11})(\eta^6\text{-}1,3,5\text{-cyclooctatriene})]^+$ (2) and $[\text{RuH}(\text{COD})\text{L}_3]^+$ (5) (COD = cycloocta-1,5-diene, L = PMe_2Ph , AsMePh_2) are convenient precursors to a range of η^5 -dienyl complexes of ruthenium(II); evidence for hydrogen transfer processes is presented.

In extension of our studies of the interaction of dienes and polyenes with cationic ruthenium hydride complexes [1,2], we have discovered synthetic routes to a range of cationic dienyl complexes which are formed through unusual hydrogen-transfer processes. The reactions studied are illustrated in Scheme 1. The results are pertinent to the few previous reports of hydrogen transfer between coordinated olefin ligands promoted by Ru [4,5], Rh and Ir [6] and Mo [7] complexes.

Treatment of acetone or methanol solutions of $[\text{RuH}(\text{COD})(\text{NH}_2\text{NMe}_2)_3][\text{PF}_6]$ (1) (COD = cycloocta-1,5-diene) [3] with excess cyclooctatetraene gives in 30% yield a yellow product of stoichiometry $[\text{Ru}(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})][\text{PF}_6]$. Variable temperature NMR studies show that although the compound is fluxional, it can be completely assigned as $[\text{Ru}(1-3:5,6-\eta\text{-C}_8\text{H}_{11})(\eta^6\text{-}1,3,5\text{-cyclooctatriene})][\text{PF}_6]$ (2) from the $^{13}\text{C}^*$ and selective $^1\text{H}\{^1\text{H}\}$ spectra at -80°C . [8] The observed changes on warming the sample have not been fully elucidated, but are consistent with a dynamic process which involves either a change in the orientation of the triene ligand with respect to the unsymmetric dienyl moiety or an intramolecular hydrogen transfer via

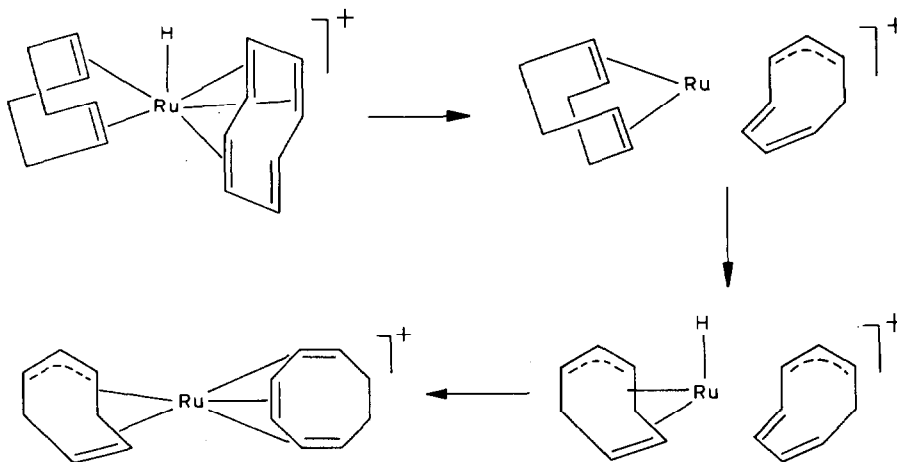
* CD_2Cl_2 , (124 MHz), δ (CH) 99.7, 97.9, 97.0, 96.9, 95.1, 93.0, 91.6, 85.8, 77.2, 44.0, 40.7 ppm;
 $\delta(\text{CH}_2)$ 36.8, 36.4, 25.4, 23.7, 18.7 ppm.



SCHEME 1 (i) COT, MeOH, 60°C; (ii) RNC, acetone, 25°C; (iii) PMe_2Ph , $\text{P}(\text{OMe})_3$, AsMePh_2 , MeOH, 60°C; (iv) dioxane, COD, 100°C.

a transient species $[\text{RuH}(\eta^6\text{-1,3,5-cyclooctatriene})_2][\text{PF}_6]$. Studies in deuterio-acetone have shown that 2 is formed through an intramolecular hydrogen transfer from COD to a coordinated COT ligand and is suggested to occur by the mechanism shown in Scheme 2 [10].

The triene ligand of 2 is readily displaced by a range of ligands including olefins, acetylenes, arenes, isocyanides, phosphines and arsines. In acetone or methanol solution 2 and isocyanides form $[\text{Ru}(1-3:5-6-\eta\text{-C}_8\text{H}_{11})(\text{RNC})_3][\text{PF}_6]$ (3) ($\text{R} = \text{Bu}^t$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$) whereas with phosphines and arsines the salts $[\text{Ru}(1-5-\eta\text{-C}_8\text{H}_{11})\text{L}_3][\text{PF}_6]$ (4) $\text{L} = \text{PMe}_2\text{Ph}$, $\text{P}(\text{OMe})_3$, AsMePh_2 ; $\text{L}_3 = (\text{Ph}_2\text{PCH}_2)_3\text{CCH}_3$) are isolated. Since the spectroscopic data for 4 did not exclude the possible formation of a bicyclic $\eta^3\text{-[3.3.0]hexahydropentalenyl}$ ligand [11] the X-ray structure of 4 ($\text{L} = \text{PMe}_2\text{Ph}$) was undertaken.



SCHEME 2

The molecular structure illustrated in Fig. 1, shows that the five approximately co-planar (within 0.04(3) Å) carbon atoms of the carbocyclic ring are bonded to the Ru(PMe₂Ph)₃⁺ fragment. Of the five ruthenium carbon distances those to C(42) and C(44) are the shortest, with the distance to the central C(43) being slightly longer (by ca. 0.04(1) Å) and those to the outer

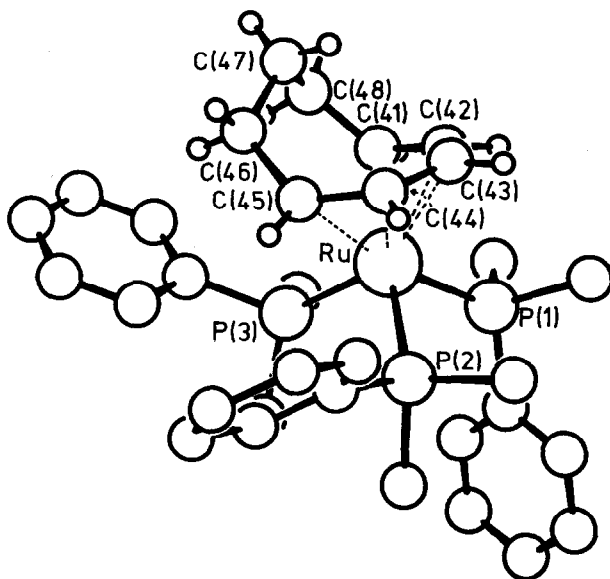


Fig. 1. A perspective view of **4** ($L = \text{PMe}_2\text{Ph}$) showing the atom numbering scheme. Selected bond lengths (Å) and angles ($^\circ$): Ru-P(1) 2.374(2), Ru-P(2) 2.356(2), Ru-P(3) 2.343(2), Ru-C(41) 2.283(8), Ru-C(42) 2.182(8), Ru-C(43) 2.226(7), Ru-C(44) 2.191(7), Ru-C(45) 2.297(7) C(41)-C(42) 1.407(11), C(42)-C(43) 1.408(11), C(43)-C(44) 1.412(11), C(44)-C(45) 1.421(11), C(45)-C(46) 1.485(11), C(46)-C(47) 1.524(12), C(47)-C(48) 1.495(12), C(48)-C(41) 1.516(11), C(48)-C(41)-C(42) 123.9(7), C(41)-C(42)-C(43) 128.7(7), C(42)-C(43)-C(44) 125.3(7), C(43)-C(44)-C(45) 127.5(7), C(44)-C(45)-C(46) 125.6(7), C(45)-C(46)-C(47) 116.0(7), C(46)-C(47)-C(48) 109.5(7), C(47)-C(48)-C(41) 117.6(7).

C(41) and C(45) being considerably longer (by ca. 0.10(1) Å). A similar trend in M—C distances was observed for the η^5 -C₈H₉ ligand in [Ru(η^5 -C₈H₉)-(1,3,5-C₆H₃Me₃)]PF₆ [12] and for the bicyclo- η^5 -C₈H₉ ligand in [Ru(η^5 -C₈H₉)(PMe₂Ph)₃]PF₆ [2], but in [Cr(η^5 -C₈H₁₁)H(PF₃)₃] the M—C distances tend to decrease from the outer to the centre carbon atoms [13]. The C—C bond lengths of the carbon atoms bonded to ruthenium are in the range 1.407—1.421(11) Å in keeping with a η^5 -dienyl framework for the ligand*.

The η^5 -salts 4 (L = PMe₂Ph, AsMePh₂) were also obtained by heating the hydridodiene complexes [RuH(COD)L₃]PF₆ in dioxane at 100°C in the presence of excess cycloocta-1,5-diene which was converted to a mixture of cyclooctene, 1,3-, 1,4- and 1,5-cyclooctadiene. The detection (GC analysis) of cyclooctene in equimolar amounts with the product 4, together with the observation that neither the 1,3- nor the 1,4- isomer of cyclooctadiene was effective, established that the 1,5-isomer acted as the hydrogen acceptor in this reaction. Surprisingly, other complexes 5 (L = PMePh₂, P(OMe)Ph₂, PMe₃ and (Ph₂PCH₂)₃CCH₃) were not converted into 4 in the presence of excess COD although these η^5 -C₈H₁₁ derivatives are accessible via 2.

No satisfactory explanation for this unusual reactivity pattern can be given at this stage, although it may be related to our previous observation [1] that the steric and electronic properties of the ligands are critical factors in the hydride transfer to coordinated olefin in 4. A clue to unravelling the mechanism is the observation that under less severe reaction conditions (MeOH, 60°C) 5 (L = PMe₂Ph) is converted into a mixture of 4 (40% yield) and the η^3 -enyl, [Ru(η^3 -C₈H₁₃)(PMe₂Ph)₃]⁺ in the time taken to isomerize the added COD completely to cycloocta-1,3-diene. Hence it seems likely that with larger ligands, where formation of the η^3 -enyl is known to be more rapid, the rate of the isomerization is much faster than that of the dehydrogenation, whereas with smaller ligands the ligand dissociation necessary to allow coordination of a second COD ligand, does not occur.

We are currently exploring the possibility of phosphine dissociation from 5 and related (tris-phosphine)ruthenium moieties by spin-saturation transfer methods in order to obtain more information on the mechanistic pathway in the formation of these η^5 -dienyl species. We have also observed that reaction of 2 with P(OMe)₂Ph gave [RuH(COD){P(OMe)₂Ph}₃]⁺ at 0°C and [RuH{P(OMe)₂Ph}₅]⁺ at 30°C. The implications of this hydrogen transfer process, which may be related to olefin disproportionation reactions observed with zirconium systems [14], are currently being investigated.

*Crystal data for 4 (L = PMe₂Ph). C₃₂H₄₄F₆P₄Ru *M* = 767.66, orthorhombic, space group *Pbca*, with *a* 23.553(4), *b* 14.965(2), *c* 19.085(3) Å, *U* 6727(3) Å³, *Z* = 8, *D_c* 1.516 Mg m⁻³, *F*(000) = 3152, μ (Mo-K α) 0.628 mm⁻¹. The structure was solved by Patterson and electron density map methods using SHELX and was refined by least-squares procedures. Anisotropic temperature factors were used for all non-H atoms; all the H atom positions were located and refined. The refinement converged with *R* = 0.0531 and *R_w* = 0.0461 for 3242 unique reflections with *F_o* > 4 σ (*F_o*) measured in the range 3 ≤ θ ≤ 23° at 293 K on a Philips PW1100 4-circle diffractometer (NPRL, CSIR), using a crystal of dimensions 0.19 × 0.18 × 0.16 mm grown from dichloromethane-ethanol solution. (The atomic coordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.)

References

- 1 T.V. Ashworth, A.A. Chalmers, E. Meintjies, H.E. Oosthuizen and E. Singleton, *Organometallics*, **3** (1984) 1485.
- 2 T.V. Ashworth, A.A. Chalmers, D.C. Liles, E. Meintjies, H.E. Oosthuizen and E. Singleton, *J. Organomet. Chem.*, **276** (1984) C19; **276** (1984) C49.
- 3 T.V. Ashworth, E. Singleton and J.J. Hough, *J. Chem. Soc., Dalton.*, (1977) 1809.
- 4 K. Itoh, H. Nagashima, T. Ohshima, N. Oshima and H. Nishiyama, *J. Organomet. Chem.*, **272** (1984) 179.
- 5 P. Pertici, G. Vitulli, M. Paci, and L. Porri, *J. Chem. Soc., Dalton*, (1980) 1961.
- 6 P.T. Dragett, M. Green, and S.F.W. Lowrie, *J. Organomet. Chem.*, **135** (1977) C60.
- 7 M.L.H. Green and P.A. Newman, *J. Chem. Soc., Chem. Commun.*, (1984) 816.
- 8 The 1-3:5-6- η -dienyl group of **2** was readily identified by comparison with the ^1H NMR spectrum of $[\text{Ru}(1-3:5-6-\eta\text{-C}_8\text{H}_{11})(\eta^6\text{-PhBF}_3)]$ [9]. We originally reported [9] **2** as containing a coordinated cyclooctatetraene ligand.
- 9 T.V. Ashworth, M.J. Nolte, R.H. Reimann, and E. Singleton, *J. Chem. Soc., Chem. Commun.*, (1977) 937.
- 10 R.F. Heck, *Organotransition Metal Chemistry, A Mechanistic Approach*, Academic Press, New York, 1974, p. 117.
- 11 G. Deganello, *Transition Metal Complexes of Cyclic Polyolefins*, Academic Press, New York, 1979, p. 390.
- 12 M.A. Bennet, T.W. Matheson, G.B. Robertson, A.K. Smith and P.A. Tucker, *Inorg. Chem.*, **20** (1981) 2353.
- 13 J.R. Blackborow, C.R. Eady, F.-W. Grevels, E.A. Koerner von Gustorff, A. Scrivanti, O.S. Wolfbeis, R. Benn, D.J. Brauer, C. Kruger, P.J. Roberts and Y.-H. Tsay, *J. Chem. Soc. Dalton*, (1981) 661.
- 14 M.B. Fischer, E.J. James, T.J. McNeese, S.C. Nyburg, B. Posin, W. Wong-Ng and S.S. Wreford, *J. Am. Chem. Soc.*, **102** (1980) 4941.