The Facile Dehydrogenation of Cyclo-octa-1,5-diene at a Ruthenium(II) Centre. The Crystal and Molecular Structure of the Novel Ruthenium(IV) 1—3-η : 5—7-η-Cyclo-octa-1,5-dienediyl Complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{10})]PF_6$, an Intermediate in the Dehydrogenation of Cyclo-octa-1,5-diene to Cyclo-octa-1,3,5-triene in $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{12})Cl]$

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The complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{12})Cl]$ (C_8H_{12} = cyclo-octa-1,5-diene) undergoes facile dehydrogenation of the cyclo-octadiene ligand in ethanol in the presence of NH_4PF_6 to give two isomeric products of stoicheiometry $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{10})]PF_6$; the first is a ruthenium(II) complex containing the cyclo-octa-1,3,5-triene ligand, and the second is a ruthenium(IV) complex containing the novel 1—3-η : 5—7-η-cyclo-octa-1,5-dienediyl ligand, a feature confirmed by *X*-ray crystallography.

Metal–allyl species are proposed as key intermediates in stoicheiometric and catalytic dehydrogenation reactions of alkenes at transition metal centres.[1,2] Almost without exception, little is known about the nature of these intermediates, and to date few have been isolated.[2] Herein we report on the unusual NH_4PF_6 promoted dehydrogenation reactions of diene ligands in the cyclopentadienylruthenium(II) complexes $[(\eta\text{-}C_5H_5)Ru(\eta\text{-diene})Cl]$, and on the isolation and structural characterization of the first ruthenium(IV)–allyl compound unequivocally shown to be an intermediate in the dehydrogenation of a diene ligand at a ruthenium centre.

Refluxing the ruthenium(II) complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{12})Cl]$ (**1**; C_8H_{12} = cyclo-octa-1,5-diene)[3] with excess of NH_4PF_6 in ethanol for 3 h gives, after filtration and cooling, an approximately 1 : 1 mixture of two crystalline products both having the stoicheiometry $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{10})]PF_6$.† The first, (**2**), containing the cyclo-octa-1,3,5-triene ligand was readily identified on the basis of characteristic ^1H and ^{13}C

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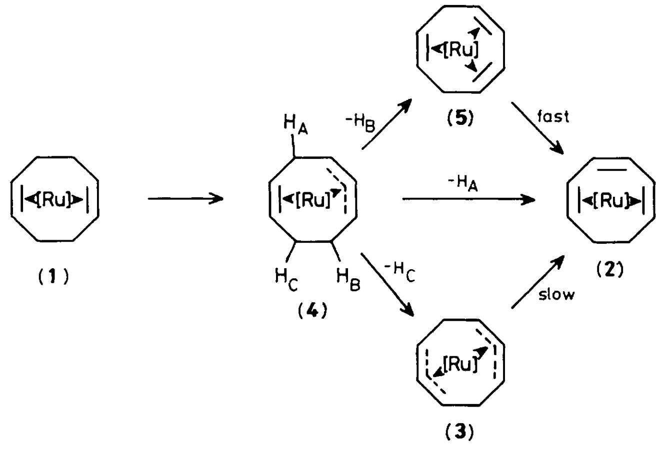
† Satisfactory elemental analyses were obtained for all new compounds.



Scheme 1. [Ru] = (η-C_5H_5)Ru(Cl).

n.m.r. signals[4] and also by an independent synthesis from (**1**) and cyclo-octa-1,3,5-triene in boiling ethanol followed by anion exchange with NH_4PF_6. In the ^1H n.m.r. spectrum of the second product, (**3**), (CD_3COCD_3, 303 K) a sharp singlet at δ 5.70 is observed for the cyclopentadienyl ligand; the remaining signals appearing at δ 4.35 [H_α, t, $J(H_\alpha\text{–}H_\beta)$ 7.3 Hz], 3.90 [$2H_\beta$, dt, $J(H_\beta\text{–}H_\gamma)$ 9.3, $J(H_\beta\text{–}H_{\gamma'})$ 7.3 Hz], 3.12 [$2H_\gamma$, dt, $J(H_\gamma\text{–}H_{\gamma'})$ 14.5 Hz], and 2.16 [$2H_{\gamma'}$, dt] are consistent with the novel 1—3-η: 5—7-η-cyclo-octa-1,5-dienediyl ligand. In the ^{13}C n.m.r. spectrum of (**3**) (CD_3COCD_3, 303 K) the cyclopentadienyl carbons appear at δ 87.25 while the carbons of the highly symmetrical C_8H_{10} ring are observed as the expected three resonances appearing at δ 79.16 (C_α), 21.05 (C_β), and 15.64 (C_γ). Complex (**3**) has no precedent in ruthenium chemistry representing the first ruthenium(IV) complex containing solely hydrocarbyl ligands[5] and the first example, as far as we are aware, of a complex containing the cyclo-octa-1,5-dienediyl ligand. For these reasons the *X*-ray crystal structure of (**3**) has been determined.‡

Both the complex cation and anion have crystallographic mirror symmetry with the two methylene carbon atoms of the C_8H_{10} ligand of the cation lying in the mirror plane (Figure 1). The ruthenium–carbon distances for the independent allyl function are 2.251(8), 2.162(8), and 2.271(7) Å; the pattern of metal–carbon bond lengths with the central one shorter than the two outer ones is typical of metal–allyl bonding in the absence of steric constraints.[7]

Heating of (**1**) with NH_4PF_6 for longer periods than 3 h, *e.g.* 12 h, gives (**2**) as the only observable product of the reaction, while heating (**1**) alone in ethanol for 3 h yields only traces of (**2**) and (**3**) and unchanged (**1**). In addition to this, (**3**) has been found to be converted into (**2**) only slowly on heating in ethanol alone (40% conversion in 12 h) but more rapidly in the presence of NH_4PF_6. These observations lead to the conclusion that (**3**) is an intermediate in the NH_4PF_6 promoted dehydrogenation of (**1**) to (**2**). Thus these reactions represent the first example of the dehydrogenation of an organic moiety at a ruthenium centre promoted by an agent such as NH_4PF_6, and the only example of the dehydrogenation of an organic moiety at a ruthenium(II) centre for which a ruthenium(IV) intermediate has unequivocally been proven.

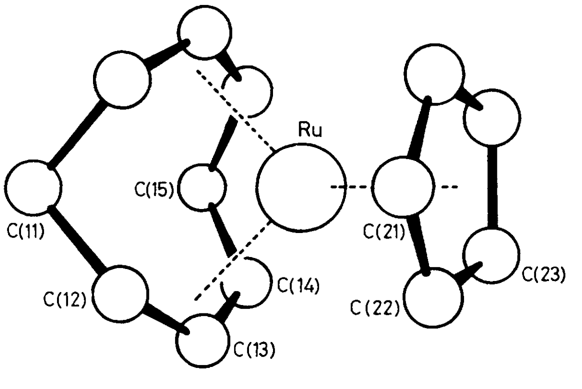


Figure 1. A perspective view of (**3**) (hydrogen atoms omitted for clarity) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru–C(12) 2.251(8), Ru–C(13) 2.162(8), Ru–C(14) 2.271(7), Ru–C(21) 2.158(16), Ru–C(22) 2.149(11), Ru–C(23) 2.251(9), C(11)–C(12) 1.470(10), C(12)–C(13) 1.362(10), C(13)–C(14) 1.397(9), C(14)–C(15) 1.513(9), C(12)–C(11)–C(12′) 99.8(9), C(11)–C(12)–C(13) 130.4(9), C(12)–C(13)–C(14) 123.4(8), C(13)–C(14)–C(15) 128.2(8), C(14)–C(15)–C(14′) 100.7(7).

That we have never been able to obtain (**3**) as the sole product of the (**1**)–NH_4PF_6 reaction system, even with short reaction times and milder conditions, and that the formation of (**2**) in these reactions proceeds faster than the rate of conversion (**3**) → (**2**), leads us to conclude that there exist a number of pathways operative for the conversion of (**1**) into (**2**). Regardless of the mechanism of hydrogen abstraction from the C_8 ring, these pathways could possibly be correlated with the *site* of hydrogen abstraction (Scheme 1). Proceeding from a likely common allyl-ene intermediate[8] (**4**), loss of H_A would lead directly to (**2**). On the other hand abstraction of H_B would give the transient cyclo-octa-1,3,6-triene species (**5**) [which would be expected to be converted rapidly into (**2**) *via* a hydrogen shift mechanism[9] under the experimental conditions], while abstraction of H_C would give (**3**), which subsequently isomerizes only slowly to (**2**).

As yet we have been unable to clarify the role of NH_4PF_6 [other agents such as $NaSbF_6$ and NH_4BF_4 have also been observed to promote the formation of (**2**)], and the mechanism(s) of hydrogen transfer. However, in further investigating the formation of (**3**) from (**1**) we have found that the bis(allyl) complex can be produced in the pure form as the product of a regiospecific dehydrogenation reaction of (**1**) when (**1**) is treated with an equivalent of either $AgPF_6$ in ethanol at room temperature, or NH_4PF_6 in hot ethanol in the presence of a hydrogen acceptor, *e.g. trans,trans,trans*-cyclododeca-1,5,9-triene. Reaction of (**1**) with HPF_6 in ethanol at room temperature also produces (**3**) in moderate (*ca.* 40%) yield, but in this case contaminated by several as yet unidentified products. Deuteriation studies are currently in progress which might help to clarify further some of the mechanistic issues.

The cyclo-octa-1,5-diene ligand in (**1**) is readily displaced by other diene systems[3] and related dehydrogenation reactions of these ligands have also been observed. Thus, for instance, [(η-C_5H_5)Ru(η-C_6H_8)Cl] (C_6H_8 = cyclohexa-1,4-diene) and [(η-C_5H_5)Ru(η-C_7H_{10})Cl] (C_7H_{10} = cyclohepta-1,3-diene) are readily dehydrogenated in warm ethanol in the presence of NH_4PF_6 to give the cationic ruthenium(II) complexes [(η-C_5H_5)Ru(η-C_6H_6)]PF_6[10] and [(η-C_5H_5)Ru(η-C_7H_8)]PF_6[3] con-

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‡ *Crystal Data:* $C_{13}H_{15}F_6PRu$, M = 417.30, orthorhombic, space group *Pnma*, a = 13.079(4), b = 8.496(4), c = 12.777(2) Å, U = 1419.5 Å^3, D_c = 1.952 Mg m^{-3} for Z = 4, $F(000)$ = 824, Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 1.138 mm^{-1}. The structure was solved by conventional heavy atom methods and was refined by weighted least squares methods [$w = 1/\sigma^2(F_o)$] using SHELX[6] to give a current R = 0.0578 and R_w = 0.0517 for 1152 reflections with $F_o \geq 4\sigma(F_o)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

taining the benzene and cyclohepta-1,3,5-triene ligand respectively. No intermediates were detected in these processes, and the reactions did not occur to any appreciable extent in ethanol alone.

In conclusion, the results presented here serve to highlight a hitherto unanticipated pathway for the dehydrogenation of organic substrates bound at transition metal centres,[11] and to emphasise the importance of ruthenium(IV) intermediates[12] in the activation of C–H bonds. The surprising stability of the ruthenium(IV) complex (**3**) is a notable feature which should have far reaching implications for currently held views on ruthenium(IV) organometallic chemistry.

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