Facile Organo-ruthenium(II) Redox Reactions with Cyclic Allyl Halides. The Characterization of a Novel Ruthenium(IV) Intermediate in the Dehydrohalogenation and Dehydrogenation of 3-Bromocyclohexene and the X-Ray Crystal Structure of [(η-C$_5$H$_5$)Ru(η-C$_4$H$_4$OMe)Cl$_2$]

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Reaction of [(η-C$_5$H$_5$)Ru(η-C$_8$H$_{12}$)X] (X = Br or Cl; C$_8$H$_{12}$ = cyclo-octa-1,5-diene) with the cyclic allyl halides 3-bromocyclohexene and *cis*-3,4-dichlorocyclobutene in alcohol solvents gives the ruthenium(IV) allyl complexes [(η-C$_5$H$_5$)Ru(η-C$_6$H$_9$)Br$_2$] and [(η-C$_5$H$_5$)Ru(η-C$_4$H$_4$OMe)Cl$_2$], the former being readily converted into the arene ruthenium(II) cation [(η-C$_5$H$_5$)Ru(η-C$_6$H$_6$)]$^+$; the X-ray crystal structure of [(η-C$_5$H$_5$)Ru(η-C$_4$H$_4$OMe)Cl$_2$] has been determined. ·

The dehydrogenation of organic halides is a commercially important reaction.[1] While a number of transition metals[2] and metal oxides[3] function as catalysts, few transition metal complexes are known to participate.[4] Herein we describe the unusual oxidative addition of thermolabile cyclic allyl halides at the ruthenium(II) centre in the labile cyclopentadienyl-ruthenium(II) complexes [(η-C$_5$H$_5$)Ru(η-C$_8$H$_{12}$)X] (C$_8$H$_{12}$ = cyclo-octa-1,5-diene; X = Cl or Br)[5] which in the case of 3-bromocyclohexene gives a unique insight into the dehydrohalogenation of organic halides at a transition metal centre.

Treatment of [(η-C$_5$H$_5$)Ru(η-C$_8$H$_{12}$)X] (**1**, X = Br)[5] with excess of 3-bromocyclohexene in ethanol (40 °C; 2 min) rapidly gives the ruthenium(IV) cyclohexenyl complex [(η-

C$_5$H$_5$)Ru(η-C$_6$H$_9$)Br$_2$] (**2**) as an air-stable, orange crystalline solid in 84% yield. In the ^{1}H n.m.r. spectrum of (**2**) (CD$_2$Cl$_2$; 303 K), a sharp singlet is observed for the cyclopentadienyl ligand at δ 5.27; the expected triplet for the central allyl proton appears at δ 5.23, while the remaining ring protons resonate as multiplets at δ 6.04 (2H), 2.73 (2H), and 1.60 (4H). However, it is the ^{13}C n.m.r. spectrum (CD$_2$Cl$_2$; 303 K) which, on the basis of the characteristic[6] four signal pattern appearing at δ 95.50 (C$_\alpha$), 83.39 (2C$_\beta$), 27.82 (2C$_\gamma$), and 17.44 (C$_\delta$), uniquely defines the cyclohexenyl ligand system. The cyclopentadienyl ring carbons appear at δ 96.23.

Refluxing an orange ethanol solution of (**2**) rapidly (*ca.* 5 min) gives a pale yellow solution, which, on addition of

Scheme 1. X = Br.
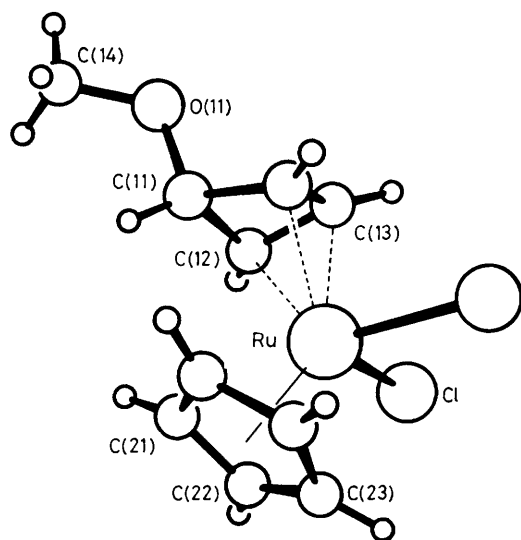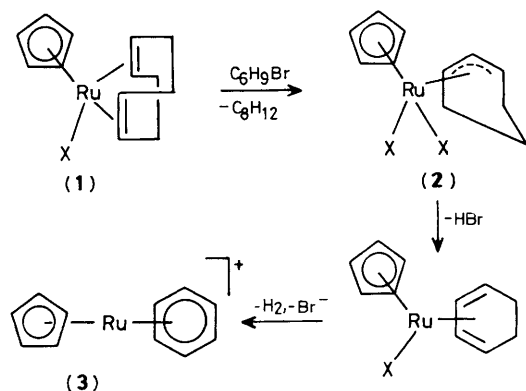
Figure 1. A perspective view of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_4H_4OMe)Cl_2]$ (**4**) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru–Cl 2.403(1), Ru–C(12) 2.181(4), Ru–C(13) 2.116(6), Ru–C(21) 2.225(4), Ru–C(22) 2.197(4), Ru–C(23) 2.175(6), C(11)–C(12) 1.526(6), C(12)–C(13) 1.423(6), C(11)–O(11) 1.422(7), O(11)–C(14) 1.415(8), Cl–Ru–Cl' 86.2(1), C(12)–C(11)–O(11) 111.3(4), C(12)–C(11)–C(12') 81.6(4), C(11)–C(12)–C(13) 90.6(4), C(12)–C(13)–C(12') 89.0(5).

NH$_4$PF$_6$ followed by cooling, deposits a crystalline precipitate of the benzene–ruthenium(II) complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_6H_6)]PF_6$ (**3**)[7] in high yield. A similar transformation of (**2**) to (**3**) can also be effected in ethanol at room temperature over a period of several hours. Complex (**3**) has been identified on the basis of its characteristic ^{1}H n.m.r. spectrum[7] and by an independent synthesis from (**1**; X = Br) and benzene in ethanol solution.[5] Complex (**3**) has also been obtained in quantitative yield by the treatment of (**1**; X = Br) with cyclohexa-1,3-diene in warm ethanol for a few minutes suggesting the sequence of steps shown in Scheme 1. This sequence represents, as far as we are aware, the only example of the spontaneous dehydrohalogenation and dehydrogenation of an organic moiety at a ruthenium(II) centre and for which a ruthenium(IV) intermediate has unequivocally been proven.

The ease of the observed oxidative addition of 3-bromo-cyclohexene to (**1**) is surprising when compared to the forcing reaction conditions recently reported by Itoh and co-workers[8] for the synthesis of the acyclic allyl complexes of the type $[(\eta\text{-}C_5R_5)Ru(\eta\text{-allyl})X_2]$ from $[(\eta\text{-}C_5R_5)RuL_2X]$ (L = CO or PPh$_3$) and allyl halides. This has prompted us to investigate further the reactions of (**1**) with thermolabile allyl halides and also with vinyl halides in order first to test the generality of the process, and secondly to gain insight into factors affecting Ru^{II} $\longleftrightarrow$ Ru^{IV} redox reactions in organometallic complexes.

For instance, *cis*-3,4-dichlorocyclobutene readily reacts with (**1**; X = Cl) in warm methanol to give, on cooling, red crystals of the ruthenium(IV) complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_4H_4OMe)Cl_2]$ (**4**) (yield 91%).† Complex (**4**) has no precedent in ruthenium chemistry[9] (although related cyclobutenyl ligand systems have been observed in, *e.g.*, palladium–acetylene chemistry[10]), and closely resembles the proposed intermediate in the formation of cyclobutadiene complexes from the dihalogenocyclobutene route.[11] For this reason, the *X*-ray crystal structure of (**4**) has been determined.‡

The molecule has crystallographic mirror symmetry; the ruthenium atom is co-ordinated by two mutually *cis* chloro ligands, an η^5-cyclopentadienyl ligand, and the unusual η^3-4-methoxycyclobutenyl ligand (Figure 1). The enyl function of the cyclobutenyl ligand is symmetrically bonded to ruthenium atom with the shorter Ru–C bond being that to the central carbon atom [2.116(6), central; 2.181(4) Å, outer carbons]. The Ru–C bond lengths are, however, consistently shorter than the observed range for ruthenium(II)–allyl bond lengths[12] (2.130—2.143 central, 2.188—2.258 Å outer).

Perhaps the most remarkable illustration of the propensity to form ruthenium(IV)–allyl complexes is the reaction of (**1**) with vinyl halides. Treatment of (**1**; X = Cl) with 1-chloro-2-methylprop-1-ene in boiling ethanol for 2 h gives a high yield of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}CH_2CMeCH_2)Cl_2]$ characterized by elemental analysis and ^{1}H n.m.r. spectroscopy,§ and independently synthesized by the direct reaction between (**1**; X = Cl) and 2-methyl-3-chloropropene for 1 min. The oxidative addition–rearrangement reaction of the vinyl halide is thus approximately 100 times slower than the oxidative addition of the analogous allyl halide. This is in keeping with the general observation that while allyl halides readily oxidatively add to a wide range of transition metal centres to give either σ- or π-allyl complexes,[13] vinyl halides are not especially reactive and rare examples of oxidative additions (giving σ-vinyl complexes) are generally to be found only in electron-rich d^{10}

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† Compound (**4**), ^{1}H n.m.r. in CD$_2$Cl$_2$: δ 5.94 (1H, m), 5.86 (5H, s, C$_5$H$_5$), 5.28 (2H, m), 3.59 (1H, m), and 2.72 (3H, s, OMe).

‡ *Crystal data:* C$_{10}$H$_{12}$Cl$_2$ORu, M = 320.18; orthorhombic, space group *Pnma*, a = 11.4550(16), b = 9.3380(13), c = 9.8942(12) Å, U = 1058.35 Å^3, Z = 4, D_c = 2.009 Mg m^{-3}, $F(000)$ = 632, Enraf-Nonius CAD4F diffractometer, Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 1.797 mm^{-1}. The structure was solved by normal heavy-atom methods and was refined by weighted least-squares [w = $1/\sigma^2(F_o)$]. Anisotropic thermal parameters were used for all non-hydrogen atoms. All hydrogen atoms were located and refined. The refinement converged with R = 0.0380 and R_w = 0.0354 for 1306 unique empirical-absorption-corrected reflections with $F_o \geqslant 4\sigma(F_o)$.

The atomic co-ordinates for this work 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.

§ ^{1}H N.m.r. in CDCl$_3$: δ 5.26 (5H, s, C$_5$H$_5$), 4.04 (2H, s), 3.69 (2H, s), and 2.21 (3H, s, Me).

systems.[14] The thermal rearrangement of σ-vinyl to π-allyl ligands has been observed to occur at iridium,[15] zirconium,[16] and molybdenum[17] centres. In each case hydrido-allene intermediates were implicated and it is thus noteworthy that the lack of β-vinylic and β-allylic protons in this ruthenium system precludes a mechanism involving a π-allene intermediate.

In conclusion, the results presented here lead us to suggest that an important criterion in the formation and isolation of stable organometallic ruthenium(IV) complexes from ruthenium(II) precursors relates to ligand competition in the co-ordination sphere of the metal. Specifically complex (1) and its congeners, containing readily displaceable, poorly competing, dialkene ligands [and therefore reacting as the pseudo 14-electron fragments $\{(\eta\text{-}C_5R_5)RuX\}$] present a facile gateway to the virtually unexplored organometallic chemistry of the ruthenium(IV) oxidation state.

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