Stoicheiometric Dehydrogenation of Cyclic Alkenes without Hydrogen Acceptors using the '$(C_5Me_5)Ru^+$' Fragment. *X*-Ray Crystal Structure of $[(\eta^5\text{-}C_5Me_5)Ru\text{-}(\mu_2,\ \eta^5,\eta^5\text{-}C_5Me_4OH)\text{-}Ru(\eta^5\text{-}C_5Me_5)]CF_3SO_3\cdot CH_2Cl_2$

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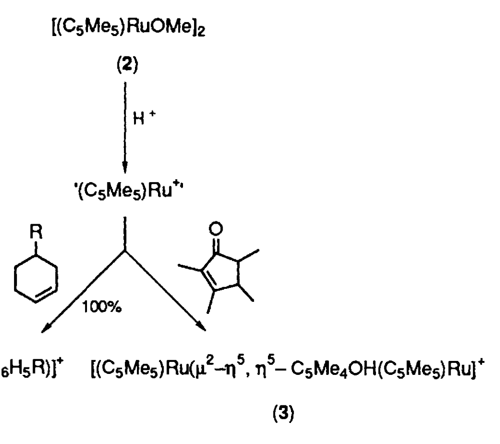
The reaction of $[(C_5Me_5)Ru(OMe)]_2$ (**2**) with CF_3SO_3H in the presence of cyclic alkenes (cyclohexene or 4-methylcyclohexene) affords the π-arene derivatives $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]CF_3SO_3$ (**4**) and $[(C_5Me_5)Ru(\eta^6\text{-}C_5H_5Me)](CF_3SO_3)$ (**5**) in 40—60% isolated yield (100% spectroscopic yield) while the same reaction with tetramethylcyclopentenone affords the novel triple-decker title complex (**3**) in 90% yield; a mechanism involving unstable dihydrogen intermediate complexes is proposed.

Numerous systems are now available to activate carbon–hydrogen bonds, a number of which are even able to functionalize saturated hydrocarbons.[1] Concerning the dehydrogenation of hydrocarbons, this reaction can be conducted either photochemically[1e,2,3] or thermally in the presence of hydrogen acceptors.[1b,4,5] The latter procedure can be applied under milder conditions to the catalytic dehydrogenation of cyclohexene (80 °C).[6]

We have recently reported that the protonation of $[(C_5Me_5)RuH_3(PCy_3)]$ (Cy = cyclohexyl) at low temperature led to the evolution of three moles of H_2 and formation of $[(C_5Me_5)Ru(C_6H_9PCy_2)]BF_4$.[7] Considering PCy_3 as an alkane possessing a function enabling it to approach the '$(C_5Me_5)Ru^+$' fragment, it was of interest to see whether other 'functional alkanes' could thus be dehydrogenated. We focused first on cyclic alkenes because upon dehydrogenation they would lead to aromatic hydrocarbons for which '$(C_5Me_5)Ru^+$' is known to have a great affinity.[8] Furthermore



Scheme 1

aromatization of cyclohexene is not an easy process[6] and if this reaction could be performed under mild conditions (room temperature or below) it could be employed for synthetic purposes provided that the aromatic product could be easily recovered.

We now describe the facile aromatization at room temperature of tetramethylcyclopentenone, cyclohexene, and 4-methylcyclopentene and the *X*-ray crystal structure of the triple-decker complex $[(C_5Me_5)Ru(\mu_2\text{-}\eta^5,\eta^5\text{-}C_5Me_4OH)Ru(C_5Me_5)]CF_3SO_3$.

We have shown recently that the fragment '$(C_5Me_5)Ru^+$' prepared either by zinc reduction of $[(C_5Me_5)RuCl_2]_n$ (**1**)[8c] or protonation of $[(C_5Me_5)Ru(OMe)]_2$[8d] reacted readily with aromatic hydrocarbons, including polyfunctional ones like pyridine or other nitrogen heterocycles, diphenylacetylene, or benzoic acid to give π-arene adducts. We applied the latter procedure first to tetramethylcyclopentenone which was likely to lead to a modified ruthenocene. Thus, the reaction of (**2**) with CF_3SO_3H in CH_2Cl_2 at room temperature in the presence of tetramethylcyclopentenone (1 equiv.) led, after recrystallization from CH_2Cl_2–Et_2O, to yellow crystals (90% yield based on ruthenium) of a complex identified by microanalytical and spectroscopic methods as well as by *X*-ray crystallography as $[(C_5Me_5)Ru(\mu_2\text{-}\eta^5,\eta^5\text{-}C_5Me_4OH)Ru(C_5Me_5)]$-$CF_3SO_3\cdot CH_2Cl_2$ (**3**)† (see Figure 1). The cyclic and exocyclic C–C bonds of the C_5Me_5 as well as the Ru–C_5Me_5 bonds are normal for such compounds[8] whereas the Ru–C bonds of the C_5Me_4O ligands are *ca.* 0.06 Å longer than the corresponding Ru–C_5Me_5 bonds [mean value 2.223(3) Å compared to 2.159(3) Å].

The cyclic C–C bonds of C_4Me_4O are similarly slightly elongated [mean value 1.476(5) Å instead of 1.429 Å for C_5Me_5] but the most interesting feature is the presence of a long C–O bond [1.366(3) Å] typical of a single bond. The hydroxo proton [O(1)–H(1) 0.97(2) Å] is involved in hydrogen bonding with an oxygen atom of $CF_3SO_3^-$. The structure can thus be described as a bis-($C_5Me_5Ru^+$) adduct of the hydroxytetramethylcyclopentadienyl anion. The mechanism of this reaction is not clear. It probably implies as a first step the dehydrogenation of cyclopentanone to give cyclopentadienone. However this is followed by an apparent two-electron reduction of the organic ligand. A similar phenomenon has been observed upon reaction of '$(C_5Me_5)Ru^+$' with quinone which leads to a π-hydroquinone complex.[9] These reactions will be reported separately.

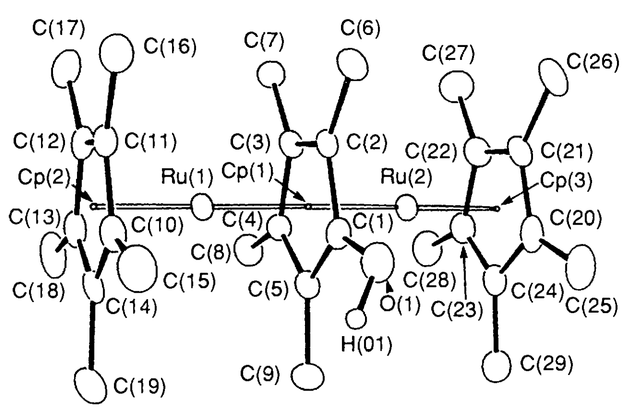


Figure 1. ORTEP view of $[(C_5Me_5)Ru(\mu^2\text{-}\eta^5,\eta^5\text{-}C_5Me_4OH)$-$Ru(C_5Me_5)]$ cation. Selected bond lengths (Å) and angles (°): Ru(1)–Cp(1) 1.830(3), Ru(1)–Cp(2) 1.783(3), Ru(2)–Cp(1) 1.840(3), Ru(2)–Cp(3) 1.787(3), Cp(1)–Ru(1)–Cp(2) 179.6(2), Cp(1)–Ru(2)–Cp(3) 179.3(2); C(1)–C(2) 1.462(5), C(2)–C(3) 1.468(5), C(3)–C(4) 1.481(5), C(4)–C(5) 1.478(5), C(5)–C(1) 1.493(5), C(1)–O(1) 1.359(4). Cp(1) is the centroid of the hydroxytetramethylcyclopentadienyl group, and Cp(2) and Cp(3) those of the pentamethylcyclopentadienyl ligands.

The dehydrogenation process is probably slow compared to co-ordination, which explains the formation of the triple-decker structure. Such structures are not unusual in organometallic chemistry,[10] but this one involves a novel hydroxytetramethylcyclopentadienyl ligand.

The reaction of $[(C_5Me_5)Ru(OMe)]_2$ with CF_3SO_3H in the presence of cyclohexene or 4-methylcyclohexene (1 equiv.) leads respectively, after recrystallization, to $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]CF_3SO_3$ (**4**) and $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_5Me)]$[11] (**5**) in 40—60% yield. For comparison, the same reaction with toluene leads to (**5**) in 60% yield. Spectroscopic yields, determined by ^1H NMR spectroscopy of reaction solutions were consistently found to be 100%. Gentle warming of the reaction solution to 40 °C (reflux in CH_2Cl_2) increases the rate of reaction but does not modify it. Finally, the dehydrogenation reaction can be carried out by adding 1 equiv. of 4-methylcyclohexene to a solution of '$(C_5Me_5)Ru^+$' prepared by dissolving (**2**) in neat CF_3CO_2H. A 100% spectroscopic yield was obtained for (**5**).

We checked by GLC analysis that hydrogen transfer had not occurred. No cyclohexane or methylcyclohexane was formed.

This is the first observation of such an intermolecular spontaneous dehydrogenation reaction.

The mechanism presumably involves initial co-ordination of the alkene and formation of a cationic hydrido allyl ruthenium(IV) derivative. Hydrogen transfer in similar complexes is well known.[12] A few years ago, we described the chemistry of such species and more specifically their great ability to undergo hydrogen transfer reactions[13] as well as the crystal structure of $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$.[14] The second step would be the formation of one mole of H_2 co-ordinated to ruthenium and elimination from a cationic ruthenium(II) centre. We have recently shown that this step is possible.[7] The second mole of H_2 would be similarly eliminated.

To conclude, the use of the '$(C_5Me_5)Ru^+$' fragment for the dehydrogenation of cyclic alkenes at room temperature is described. The absence of hydrogen acceptor and the great

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† Satisfactory microanalyses (C, H) were obtained for (**3**): ^1H NMR δ 1.73 (s, 30H, C_5Me_5), 2.35 (s, 6H, 6-H_3, 9-H_3), 2.49 (s, 6H, 7-H_3, 8-H_3), and 8.2 (s, 1H, OH) (numbering as for crystal structure).

selectivity of '$(C_5Me_5)Ru^+$' for arene co-ordination should make this method attractive in organic chemistry.

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