the nucleophilic properties of **6** are weaker than those of **3**. Complex **6** shows many physicochemical similarities to $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(O_2)$, which contains the $\mu\text{-}\eta^2\text{:}\eta^2$ coordination mode of the peroxide ion, and it is concluded that **6** also has the same particular coordination structure.

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Supplementary Material Available: Tables S-I–S-V, giving the summary of X-ray analyses, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2**, **4**·$2C_6H_6$, and **5** (26 pages); Table S-VI, listing observed and calculated structure factors for complexes **2**, **4**·$2C_6H_6$, and **5** (28 pages). Ordering information is given on any current masthead page.

Carbon–Hydrogen, Carbon–Oxygen, and Carbon–Carbon Bond Activation by an Electrophilic Ruthenium Complex

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Abstract: The "Cp^*Ru^+" fragment generated by protonation of $[Cp^*Ru(OMe)]_2$ with CF_3SO_3H reacts in CH_2Cl_2 or THF with cyclic C_6 alkenes, dienes, alcohols, ketones, enones, and diones to yield coordinated aromatic derivatives after C–H, C–O, or C–C activation. The following transformations have been performed: cyclohexene and methylcyclohexene into benzene and toluene; 1,3- or 1,5-cyclooctadiene into 1,3,5-cyclooctatriene; cyclohexanol, cyclohexanone, or cyclohexenone into benzene; methylcyclohexenone into toluene; cyclohexanedione into phenol; 4,4-dimethylcyclohexenone and isophorone into 4-methylphenol and 3,5-dimethylphenol. The byproducts of these reactions are H_2, H_2O, CH_4, and some C_2H_6. The conversions have been optimized and reach 100% for the three types of activation. The selectivity is better than 99% for C–H and C–O activation. In the case of *gem*-dimethyl enones, the formation of phenol derivatives is accompanied by the formation of their methyl ethers, but this problem can be circumvented. The mechanism of the reactions shows classical C–H activation and hydrogen-transfer processes to occur at the early stage of all the reactions. This is followed by H_2 elimination possibly through an unstable dihydrogen intermediate, H_2O elimination from a compound containing a coordinated OH group, or C–C bond breaking. The last process involves a radical pathway, as evidenced by the observation of C_2H_6 in the gaseous phase.

Introduction

Much interest has been devoted in the last decade to the activation of the carbon–hydrogen bond and to the functionalization of alkanes.[1] Several approaches have been used, including the utilization of electron-rich organometallic complexes able to insert into unactivated C–H bonds.[2] This approach has been used to develop a photochemical catalytic process for the selective functionalization of alkanes.[3] Early transition metals have been found to exhibit a different reactivity which has led to the novel concept of "σ-bond metathesis"[4] and recently to productive catalytic reactions.[5] A third approach has been the use of electrophilic platinum metal derivatives such as cationic complexes of platinum[1a] or palladium.[1e] In that case, methane activation and functionalization have even been possible.

Although numerous systems have been found to activate carbon–hydrogen bonds, much less is known about carbon–carbon bond activation. This process has been well documented in superacidic media,[6] but it has been much more difficult to observe in the presence of soluble tansition-metal complexes, whether electron rich or electrophilic.[7,8] Furthermore, it almost exclusively concerns strained hydrocarbons. However, Bercaw et al. recently demonstrated that highly Lewis acidic scandium complexes are able to catalytically isomerize hydrocarbons such as pentadienes through carbon–carbon bond cleavages.[8] Similar reactions have been found by Sen et al. using $[Pd(MeCN)_4]^{2+}$.[1e]

Concerning the carbon–oxygen bond activation, the dehydration of alcohol is a classical process in acidic media,[9] but again, C–O bond cleavage mediated by metal complexes is much more unusual. A recent example of a clean C–O bond cleavage was reported by Mayer et al.[10]

The chemistry of half-sandwich ruthenium complexes containing the pentamethylcyclopentadienyl ($Cp^* = \eta^5\text{-}C_5Me_5$) ligand has

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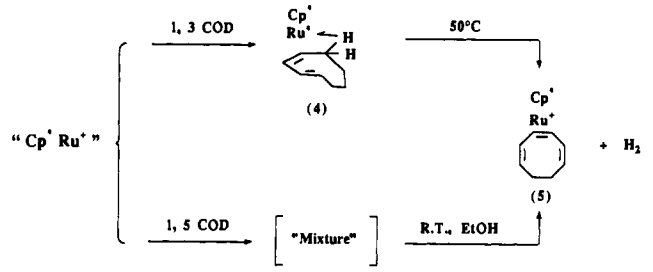
Scheme I. Reactions of "Cp*Ru$^+$" with 1,3- and 1,5-Cyclooctadiene



been increasingly studied by a number of research groups.[11-17] Thus the "Cp*Ru$^+$" fragment, which can be prepared by different methods, shows an unusual affinity for aromatic hydrocarbons. This property makes the "Cp*Ru$^+$" fragment an attractive tool for a broad range of applications, from material science[12a,b] to biology.[17]

Recently, Suzuki et al. described another aspect of the reactivity of this fragment, namely its transformation in refluxing ethanol into a μ_3-methylidyne cluster believed to proceed via C–C activation. They also mentioned a rearrangement of norbornene also involving C–C bond activation.[11c] Finally, some reactions similar to ours, i.e. dehydrogenation of 1,5-cyclooctadiene and dehydrobromation and dehydrogenation of bromocyclohexene, have been reported by Singleton et al.[18]

We have described a preparation of the "Cp*Ru$^+$" fragment and its reactivity toward various arenes and aromatic heterocycles.[16] In a separate study, we have shown that the protonation of the trihydride derivative $Cp^*RuH_3PCy_3$ leads to the loss of 3 mol of hydrogen/mol of complex and the formation of $[Cp^*Ru(C_6H_9PCy_2)]^+$, a complex containing a cyclohexenyl group and exhibiting a strong agostic interaction.[19]

These two results led us to attempt the aromatization of functionalized cyclic C_6 molecules able to approach the ruthenium center, namely alkenes, dienes, alcohols, ketones, and enones. The results of these investigations, involving C–H, C–O, and C–C bond activations, are described in this paper. The reactions with cyclohexenes have been briefly reported in preliminary communication.[20]

Results and Discussion

(1) Reactions Involving Only Carbon–Hydrogen Bond Activation. The "Cp*Ru$^+$" fragment (**1**) is prepared in CH_2Cl_2 by addition of triflic acid to the known $[Cp^*Ru(OMe)]_2$.[13a,b] A ^1H NMR study shows that this reaction yields a mixture of compounds. However, $[Cp^*Ru(\eta^6\text{-}C_6H_6)]CF_3SO_3$ (**2**) is the only product of the reaction of **1** with benzene, thus suggesting that these compounds differ only by the coordinated solvents and coordination or noncoordination of the CF_3SO_3 anion.

The reaction of "Cp*Ru$^+$" with cyclohexene or methylcyclohexene, at room temperature or 80 °C, rapidly yields **2** or $[Cp^*Ru(\eta^6\text{-}PhMe)]CF_3SO_3$ (**3**), respectively. The two reactions are quantitative and correspond to hydrogen elimination and not hydrogen transfer. Thus hydrogen is found by GC in the gas phase of the reaction (see Experimental Section) but no cyclohexane (or methylcyclohexane) is formed. In the latter case, a small amount of methane (ca. 4% as compared to H_2) is also found in the gas phase. This suggests the presence of a competitive although minor carbon–carbon bond activation process (vide infra). The same reaction with cyclohexadiene is rapid even at −80 °C and quantitatively yields **2**.

With 1,3- or 1,5-cyclooctadiene, a similar but slower reaction was expected because no aromatic species can be produced. Furthermore, Singleton et al. described the reaction of $(\eta^5\text{-}C_5H_5)RuCl(\eta^4\text{-}C_8H_{12})$ in refluxing ethanol in the presence of NH_4PF_6.[18b] Two isomers of formula $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_{10})]PF_6$ were obtained. One was a Ru(IV) derivative containing a bis(allyl) moiety whereas the other one was a Ru(II) cyclooctatriene complex. We find that the reaction of **1** with 1,3-cyclooctadiene yields at room temperature the known fluxional compound $[Cp^*Ru(1,3\text{-}C_8H_{12})]CF_3SO_3$ (**4**), which exhibits an agostic interaction involving a methylene group.[21] Gentle warming of a solution of **4** in ethanol leads to H_2 elimination and formation of the new complex $[Cp^*Ru(\eta^6\text{-}C_8H_{10})]CF_3SO_3$ (**5**) (see Scheme I). The complex was characterized by usual analytical and spectroscopic methods (see Experimental Section). In particular, the cyclooctatriene is found by ^1H NMR spectroscopy at δ 6.61 (dd, 2 H, H_1), 5.45 (m, 2 H, H_2), 5.26 (m, 2 H, H_3), 2.29 (m, 2 H, H_4 exo), and 0.97 (m, 2 H, H_4 endo) and the Cp* ligand at δ 2.04 (s, 15 H). The ^{13}C NMR spectrum also clearly demonstrates the proposed structure: δ 101.07 (C_1), 99.72 (C_5Me_5), 93.50 (C_2), 91.62 (C_3), 33.55 (C_4), 8.69 ($C_5\mathit{Me}_5$). Note that the high chemical shift of H_1–H_3 and C_1–C_3 is in agreement with a large electron delocalization in this molecule. When the same reaction is carried out with 1,5-cyclooctadiene at room temperature, a mixture of two compounds is obtained. The minor one is **5** whereas the major one, **6**, transforms into **5** simply by recrystallization from ethanol. Compound **6** was not fully characterized but was shown by NMR spectroscopy neither to contain a hydride nor to exhibit an agostic interaction. It is therefore probably similar to Singleton's bis(allyl) complex.[18b] The mechanism of these reactions will be discussed in a separate section (vide infra).

(2) Reactions Involving Carbon–Oxygen Bond Activation. After the demonstration of the facile dehydrogenation of cyclic C_6 olefins, the method was extended to functionalized olefins with the aim of preparing directly functionalized arenes.

Thus "Cp*Ru$^+$" reacts rapidly at room temperature with cyclohexenone and methylcyclohexenone. Surprisingly, no hydrogen is found in the reaction gases as evidenced by GC and instead of the expected phenol derivatives, compounds **2** and **3** are again isolated nearly quantitatively. In the case of methylcyclohexenone, some methane is found by GC which demonstrates a competition between C–O and C–C bond activation. In both cases H_2O is produced during the reaction and detected by GLC.

This result indicates the preference for dehydration rather than dehydrogenation in these systems. This can be due to two effects.

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Scheme II. Proposed Mechanism for the Dehydrogenation of Cyclic Alkenes

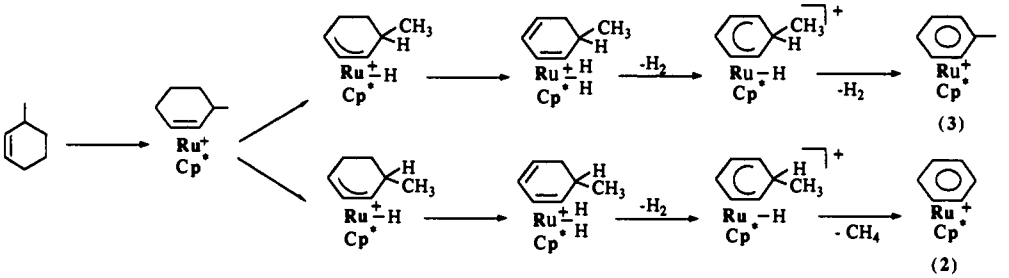


Table I. Representative C–H, C–O, and C–C Activation Reactions by the "Cp*Ru$^+$" Fragment

substrate	solvent	temp, °C	time, h	gas	conv, %	product	selectivity, %
c-C_6H_{10}	CH_2Cl_2	20	72	*a*	59	C_6H_6	100
c-$C_6H_9CH_3$	CH_2Cl_2	80	18	H_2	100	$C_6H_5CH_3$	>90
				CH_4			
c-C_6H_8	CH_2Cl_2	-80	1	*a*	100	C_6H_6	100
c-$C_6H_{11}OH$	CH_2Cl_2	80	18	*a*	≤1	C_6H_6	
c-$C_6H_{11}OH$	THF	100	22	H_2	100	C_6H_6	100
c-C_6H_{10}(=O)	CH_2Cl_2	80	24	H_2	<10	C_6H_6	
c-C_6H_{10}(=O)	THF	100	20	*a*	30	C_6H_6	80
1,4-c-C_6H_8(=O)$_2$	THF	80	16	H_2	100	C_6H_5OH	100
c-C_6H_8(=O)	CH_2Cl_2	80	21	*b, c*	100	C_6H_6	100
c-C_6H_8(=O)	CH_2Cl_2	20	1.5	*a*	100	C_6H_6	100
3-CH_3-c-C_6H_7(=O)	CH_2Cl_2	20	18	CH_4	100	$C_6H_5CH_3$	>90
3-CH_3-c-C_6H_7(=O)	CH_2Cl_2	80	18	*a*	100	$C_6H_5CH_3$	>90
1-OCH_3-c-C_6H_9	THF	100	24	*a*	100	C_6H_6	100
4,4-$(CH_3)_2$-c-C_6H_6(=O)	CH_2Cl_2	50	20	CH_4	40	4-$CH_3C_6H_4OH$	60
						4-$CH_3C_6H_4OMe$	40
4,4-$(CH_3)_2$-c-C_6H_6(=O)	THF	80	18	CH_4	90	4-$CH_3C_6H_4OH$	80
				C_2H_6		4-$CH_3C_6H_4OMe$	20
3,5,5-$(CH_3)_3$-c-C_6H_5(=O)	CH_2Cl_2	90	15	CH_4	60	3,5-$(CH_3)_2C_6H_3OH$	30
						3,5-$(CH_3)_2C_6H_3OMe$	50
3,5,5-$(CH_3)_3$-c-C_6H_5(=O)	*d*	20	26	CH_4	<10	3,5-$(CH_3)_2C_6H_3OH$	40
						3,5-$(CH_3)_2C_6H_3OMe$	20
3,5,5-$(CH_3)_3$-c-C_6H_5(=O)	*d*	60	24	*a*	50	3,5-$(CH_3)_2C_6H_3OH$	50
						3,5-$(CH_3)_2C_6H_3OMe$	40
3,5,5-$(CH_3)_3$-c-C_6H_5(=O)	THF	90	20	CH_4	50	3,5-$(CH_3)_2C_6H_3OH$	60
						3,5-$(CH_3)_2C_6H_3OMe$	35

[a] Reaction gases were not analyzed by GC. [b] H_2O was detected by GLC. [c] No gas was detected by GC. [d] In neat substrate.

First, the rupture of a C–O bond and formation of H_2O is thermodynamically favored compared to the rupture of a C–H bond and formation of H_2. Second, the reaction probably involves first the coordination of an O–H group of a dienol to the electrophilic cationic ruthenium center. The mechanism of this reaction will be discussed in a separate section; however, it is most probable that the enone will react with ruthenium through a dienol form.

In order to extend the scope of this dehydration reaction, we examined the reactivity of "Cp*Ru$^+$" with less unsaturated molecules, e.g. a dione (two unsaturations but each different), a ketone (one unsaturation), and an alcohol (no unsaturation).

The reaction of "Cp*Ru$^+$" with 1,4-cyclohexanedione proceeds at 80 °C in THF and yields exclusively the π-phenol compound [Cp*Ru(η^6-PhOH)]CF_3SO_3 (**7**)[16b,f] and water. No hydrogen and no complex of hydroquinone are found, in agreement with the dehydration being preferred to dehydrogenation. This reaction gives evidence for a hydrogen-transfer step prior to aromatization; this step is also necessary in the case of enones (vide infra).

The reactions of cyclohexanone and cyclohexanol with "Cp*Ru$^+$" were carried out under two different conditions: at 80 °C in CH_2Cl_2 or at 100 °C in THF. We found that CH_2Cl_2 itself reacts slowly with "Cp*Ru$^+$" to give a mixture of two μ_3-methylidine clusters: $[(Cp^*Ru)_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}CH)]^+$ (**8**) and $[(Cp^*Ru)_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}CO)(\mu_3\text{-}CH)]^{2+}$ (**9**). The preparation and reactivity of these clusters as well as the crystal structure of **8** will be reported separately. Compound **8** was mentioned by Suzuki et al. in a preliminary communication.[11c] By contrast, we verified that no activation reaction occurs between "Cp*Ru$^+$" and THF even at 100 °C for 24 h. In particular, no H_2 and no CH_4 are formed, only a very small amount of higher hydrocarbons (C_2, C_3, C_4, C_5, ...). However, a mixture of complexes is observed in the ^1H NMR spectrum that correspond most probably to formulations of the type [Cp*Ru(solvent)$_x$(CF_3SO_3)], which were not elucidated.

The reaction of cyclohexanone with "Cp*Ru$^+$" in CH_2Cl_2 at 80 °C for 24 h yields **2** in ca. 10% yield. Hydrogen is produced during this reaction, as expected. Under the same conditions, the reaction of cyclohexanol yields traces of **2** (≤1%). If the reactions are carried out at 100 °C in THF, the yields of **2** starting from cyclohexanone and cyclohexanol are respectively ca. 30% and ca. 100%. In the latter case, a very significant production of H_2 was detected by GC, as expected. These results, contradictory at first sight, can be rationalized as follows. In CH_2Cl_2, both compounds have access to the coordination sphere of ruthenium; the more unsaturated one will compete more successfully with CH_2Cl_2 activation. In THF, competition for coordination will occur prior to the activation step. The alcohol will be a much better ligand for the electrophilic ruthenium center than the ketone.

(3) Reactions Involving Carbon–Carbon Bond Cleavage. We mentioned earlier in this paper that the reaction of "Cp*Ru$^+$" with methylcyclohexene or methylcyclohexenone produced some methane. This was especially important in the case of methylcyclohexene, where we found ca. 4% methane as compared to hydrogen by GC. The absence of methane in the gas phase of the reaction with cyclohexene and cyclohexenone was verified.

This observation indicates that C–C activation is possible in the presence of "Cp*Ru$^+$". The results obtained with methylcyclohexene correpond to ca. 8% yield for the C–C activation reaction as compared to the C–H activation and thus tend to prove that C–C activation should be facile.

We carried out the reaction of "Cp*Ru$^+$" with *gem*-dimethylcylohexyl derivatives because, in that case, C–C bond activation is necessary for the aromatization process to occur.

"Cp*Ru$^+$" reacts with 4,4-dimethylcyclohexen-1-one or isophorone in CH_2Cl_2 to yield respectively a mixture of [Cp*Ru(η^6-4-MeC_6H_4OH)]CF_3SO_3 (**10**) and [Cp*Ru(η^6-4-MeC_6H_4OMe)]CF_3SO_3 (**11**), and a mixture of [Cp*Ru(η^6-3,5-$Me_2C_6H_3OH$)]CF_3SO_3 (**12**) and [Cp*Ru(η^6-3,5-$Me_2C_6H_3OMe$)]CF_3SO_3 (**13**). The yields obtained in these reactions vary as a function of the conditions (time, temperature) and are given in Table I. This table suggests three conclusions. First, the C–C activation can be carried out at room temperature, the conversion in neat isophorone being modest (ca. 10% in 1 day) but not negligible. Second, increasing the temperature or the reaction time does not increase the conversion; on the contrary, the conversion decreases at higher temperature. This is related to the competitive activation of CH_2Cl_2, which produces inert stable clusters (vide supra). Third, the C–C activation reaction does not cleanly produce a phenol compound but a mixture of phenol and anisole derivatives, the latter being sometimes predominant. This fact will be discussed in the following section. Authentic samples of compounds **10–13** were prepared by a procedure similar to that used for the preparation of [Cp*Ru(η^6-PhOH)]CF_3SO_3 and [Cp*Ru(η^6-PhOMe)]CF_3SO_3[16f] (see Experimental Section).

The same reaction occurs in THF at 80 °C with a better conversion (>90% for 4,4-dimethylcyclohexen-1-one, 60% for isophorone) and also better selectivities for the phenol derivatives (Table I).

The gas phase was found to contain the expected amount of methane, little if any hydrogen, but very surprisingly ca. 10% ethane as compared to methane. We verified that the ethane did not come from the solvent CH_2Cl_2 or THF and thus that it was produced during the reaction. This observation strongly suggests a radical pathway for the C–C activation step.

Finally it is worth noting a conversion of better than 90% for a selective C–C activation reaction involving 4,4-dimethylcyclohexenone.

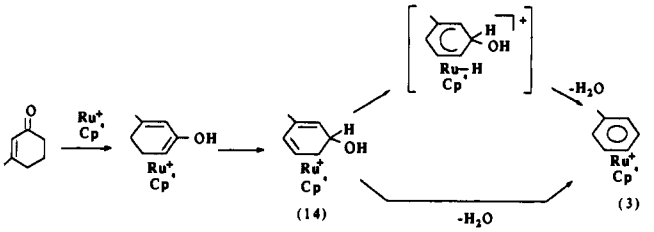
(4) Mechanistic Studies. In addition to the reactions described above and in particular to those of dienes, we followed the reactions of methylcyclohexenone and 4,4-dimethylcyclohexenone by allowing the reaction to proceed at room temperature in an NMR tube and then freezing the tube at −80 °C for observation. With methylcyclohexenone, we clearly observed the formation of **2** and the appearance of a broad peak at δ 3.97, which could be due to water.

Although the reaction was not clear, we did observe the intermediate formation of a new compound characterized by a single resonance for Cp* at δ 2.00 and broad peaks at δ 7.05 and 5.67 in a roughly 1:2 ratio. No agostic interaction and no hydride were observed during this reaction. It seems likely that this intermediate (**14**) could contain a 1,3-cyclohexadienyl ligand substituted by a methyl and a hydroxo group; see Scheme III. The hydroxo group could be coordinated to ruthenium. The chemical shifts would be in agreement with this proposal.

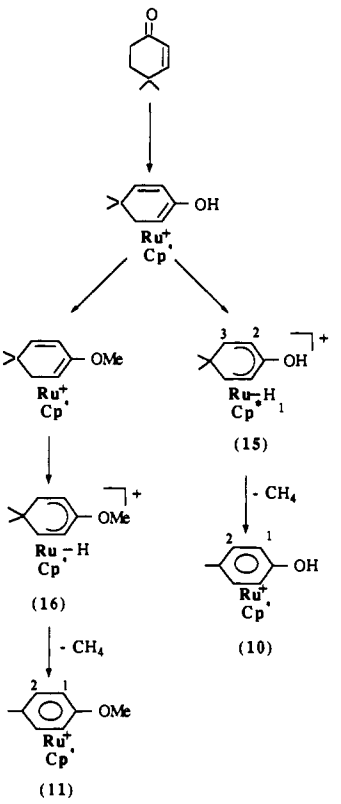
The reaction with *gem*-dimethylcyclohexenone was much clearer. We observed the immediate formation of a mixture of two compounds (**15** and **16**) that appeared to be very similar. A hydride was observed in the ^1H NMR spectra of **15** and **16**, respectively, at δ −7.19 (t, J_{HH} = 7.4 Hz) and −8.13 (t, J_{HH} = 9.7 Hz). In addition, both complexes showed two types of methyl groups near δ 0.5 and 1.2 (methyl groups endo and exo, respectively), a Cp* signal at δ 1.89, and olefinic protons near δ 2.9 (t or dd) and near δ 4.9 (d). Decoupling experiments demonstrated that the hydrides (H_1) are coupled to the protons near δ 2.9 (H_2); these protons are additionally coupled to the one near 4.9 ppm (H_3) (see Scheme IV and Experimental Section for exact values). Furthermore, one of the two complexes (**16**) showed a single resonance at δ 4.00, attributed to a C–O*Me* group. These data clearly confirm that the enone was transformed into a dienol group (**15**) or its methyl ether derivative (**16**) (see Scheme IV) upon coordination to ruthenium and activation of a C–H bond.

Interestingly, the formation of the methoxo derivative occurred very rapidly at the early stage of the reaction. The formation of these methoxo derivatives occurred then most probably through

Scheme III. Proposed Mechanism for the Dehydration of Cyclic Enones



Scheme IV. Proposed Mechanism for the C–C Activations Showing the Structure of Compounds **10**, **11**, **15**, and **16**



reaction of acid dienol derivatives with methanol present in the medium.

When the reaction was allowed to proceed for a long period of time in the NMR tube (up to 3 days), we could follow the transformation at room temperature of **15** and **16** into **10** and **11**, respectively. Interestingly again, we observed that the reaction of **16** to give **11** was more rapid than that of **15** to give **10**. This is probably related to the strong electron-releasing effect of the methoxo group.

In summary, these experiments provide a satisfactory proposal for the mechanism of these unusual C–H, C–O, and C–C activation reactions.

In the case of alkenes (see Schemes I and II), an agostic interaction follows the coordination step. Activation of a C–H bond to form a hydrido allyl type compound is likely and has been demonstrated in the case of **15** and **16**. The key step is probably the formation of an unstable (dihydrogen)ruthenium complex and elimination of H_2. However, we have no direct evidence for the formation of such a derivative.

In the case of ketones or enones, the first step is probably the coordination of the corresponding enol (e.g. dienol) to ruthenium (see Scheme III). Again, the formation of **14–16**, strongly supports this proposal. It is well-known that cationic organometallic ruthenium complexes are very active for reactions involving transfer of hydrogen. Thus, isomerization would occur to allow the hydroxo group to approach the electrophilic ruthenium center. Aroma-

tization would then occur simply by dehydration.

The isomerization process is not possible when two methyl substituents are present on the same carbon atom. In that case, there is formation of hydrido cyclohexadienyl compounds (see Scheme IV). It is not clear why these compounds are unstable even at room temperature and transform into the corresponding arenes, since even for thermodynamically favorable C–C activation reactions the kinetic barriers are usually very high.[7d] However, the observation of ca. 10% ethane as compared to methane in the gas phase demonstrates that the final step of the aromatization involves a free-radical reaction.

The NMR experiment carried out with 4,4-dimethylcyclohexenone suggests that a methyl ether derivative is generated during the very early stage of the reaction, prior to the formation of the η^5-cyclohexadienyl group, since at that stage the relative proportions of the hydroxo and methoxo derivatives no longer vary. It is most probably the very acid dienol which will react with methanol. In the case of cyclohexanone and cyclohexenones, the formation of methoxo derivatives is also possible. This would lead to the release of water in the medium, as in the dehydration reaction. We verified that methoxycyclohexene is transformed quantiatively into benzene upon reaction with **1** and thus that the formation of methyl ethers will not change the C–O activation reaction.

Conclusions

This paper describes aromatization reactions that involve C–H, C–O, and C–C activation. These reactions are unusual since they are selective and can occur at room temperature in the three cases. The reaction with alkenes is a hydrogen-elimination reaction and not a hydrogen-transfer one. When in competition, C–O activation is favored as compared to C–H activation, probably as a result of oxygen coordination to ruthenium. As expected, C–C activation is the most difficult but can nevertheless be effective as a minor process in competition with C–H or C–O activation. The aromatization step, at least in the case of C–C activation, involves a radical pathway.

The byproducts of the reactions are H_2, H_2O, CH_4, and some C_2H_6, which should make this method attractive in organic chemistry. Recovery of ruthenium is possible. Mann et al. have demonstrated the possibility for arene substitution on "CpRu$^+$" moieties (Cp = C_5H_5, C_5Me_5).[14] However this process is not catalytic yet.

The conversion can be rendered quantitative (or nearly) in the three cases. The only selectivity problem concerns the formation of anisole derivatives during the C–C activation process, due to the presence of free methanol in the reaction mixture. This however could be transformed into an advantage, since the reaction could produce in one step different aromatic ethers in the presence of excess various alcohols. In any case, the problem can be circumvented by preparing "Cp*Ru$^+$" through reaction of $[Cp^*Ru(OMe)]_2$ with $Me_3SiSO_3CF_3$. We are presently looking at applications of these reactions in various fields of organic chemistry.

Experimental Section

All operations were carried out under argon by using standard Schlenk tube techniques. Activation experiments were carried out in closed Fischer-Porter bottles equipped with Swagelok fittings that can connect directly to an injection valve of an IGC 16 Intersmat GC.

Separation of H_2, CH_4, C_2H_6, and Ar was performed on a $^1/_8$-in. column: molecular sieve 5 Å (2 m); temperature 100 °C; carrier gas He, 20 mL/min; detector TCD; sample loop 0.3 mL.

Separation of H_2O and CH_2Cl_2 was performed on a $^1/_8$-in. Porapak Q column (2 m): temperature 150 °C; carrier gas He, 20 mL/min; detector TCD; sample size 0.4 μL of solution. CH_2Cl_2 was used as internal standard.

Compounds **2** and **3** were identified by comparison with literature data[11b,12b,14b] and authentic samples. The yields of the reactions were determined by both integration in GC and integration in NMR spectroscopy.

Activation Reactions. A typical activation reaction was carried out by the following procedure: To a mixture of "Cp*Ru$^+$" (prepared from $[Cp^*Ru(OMe)]_2$ (140 mg, 0.26 mmol) and CF_3SO_3H (0.69 mmol, 60 μL)) in CH_2Cl_2 (5 mL) was added 4,4-dimethylcyclohexenone (70 μL, 0.52 mmol). The resulting solution was transferred into a Fischer-Porter bottle and heated for 18 h at 80 °C. After the reaction mixture was cooled, the gases were analyzed, and the solution was transferred into a Schlenk tube, evaporated to dryness, and analyzed by NMR spectroscopy.

This procedure was also used for methylcyclohexene, cyclohexanol, cyclohexanone, cyclohexenone, methylcyclohexenone, and 3,5,5-trimethyl-2-cyclohexenone (isophorone). The same procedure but in THF (5 mL) was used for the reaction of cyclohexanol, cyclohexanone, 1,4-cyclohexanedione, methoxycyclohexene, 4,4-dimethylcyclohexenone, and 3,5,5-trimethyl-2-cyclohexenone (isophorone); and the same procedure but in a Schlenk tube at room temperature was used for cyclohexene and methylcyclohexene. For yields see Table I.

Finally, this procedure was also used for the activation reaction of 4,4-methylcyclohexenone and 1,4-cyclohexanedione at −80 °C, in a NMR tube. ^{1}H NMR (THF-d_8): **15**, δ −7.2 (t, J_{HH} = 7.3 Hz, 1 H, H_1), 0.51 (s, 3 H, CH_3 endo), 1.21 (s, 3 H, CH_3 exo), 1.89 (s, 15 H, C_5Me_5), 2.89 (t, J_{HH} = 7.3 Hz, 2 H, H_2), 4.97 (d, 2 H, H_3); **16**, δ −8.13 (t, J_{HH} = 9.7 Hz, 1 H, H_1), 0.50 (s, 3 H, CH_3 endo), 1.18 (s, 3 H, CH_3 exo), 1.89 (s, 15 H, C_5Me_5), 2.80 (dd, J_{HH} = 9.7 Hz, 6.8 Hz, 1 H, H_2), 4.00 (s, 3 H, O*Me*), 4.90 (d, J_{HH} = 6.8 Hz, 1 H, H_3).

(1) Reaction with 1,5-Cyclooctadiene. To a stirred solution of "Cp*Ru$^+$" (0.65 mmol, prepared from 200 mg of $(Cp^*RuCl_2)_n$ and 58 μL CF_3SO_3H) in 10 mL of CH_2Cl_2 was added 100 μL of 1,5-cyclooctadiene (0.81 mmol) at −70 °C. After the solution was maintained at this temperature for 15 min, it was allowed to warm to room temperature for 1 h. The solvent was then evaporated, and the residue was washed with diethyl ether (3 × 5 mL). A yellow microcrystalline powder (192 mg) was thus obtained and shown to be a mixture of two compounds. Recrystallization from ethanol/diethyl ether or dichloromethane/diethyl ether quantitatively transformed this mixture into $[Cp^*Ru(C_8H_{10})]CF_3SO_3$ (**5**). Yield: 70%. Anal. Calcd for $C_{19}H_{25}F_3O_3SRu$: C, 46.43; H, 5.13. Found: C, 45.98; H, 5.17. ^{1}H NMR (Me_2CO-d_6): δ 0.97 (m, 2 H, H_4 endo), 2.04 (s, 15 H), 2.29 (m, 2 H, H_4 exo), 5.26 (m, 2 H, H_3), 5.45 (m, 2 H, H_2), 6.61 (dd, 2 H, H_1). ^{13}C NMR (Me_2CO-d_6): 8.69 (q, 129.3 Hz, C_5Me_5), 33.55 (t, 130.6 Hz, C_4), 91.62 (d, 157.4 Hz, C_3), 93.50 (d, 168.6 Hz, C_2), 99.72 (s, C_5Me_5), 101.07 (dt, 8.8 Hz, 169.0 Hz, C_1).

(2) Reaction with 1,3-Cyclooctadiene. This reaction is the same as that for 1,5-cyclooctadiene except that 100 μL of 1,3-cyclooctadiene (0.80 mmol) in 10 mL of dichloromethane was used. After the solution was warmed at room temperature for 1 h, the solvent was evaporated to dryness and the residue was washed with diethyl ether (3 × 5 mL), affording $[Cp^*Ru(1,3\text{-}C_8H_{12})]CF_3SO_3$ (**4**). Yield: 76%. The complex when warmed at 50 °C in ethanol quantitatively converts into **5**.

Synthesis of Authentic Complexes. (1) $[Cp^*Ru(\eta^6\text{-}4\text{-}MeC_6H_4OH)]CF_3SO_3$ (10). To a stirred dichloromethane solution (10 mL) of $[Cp^*RuOMe]_2$ (110 mg, 0.20 mmol) was added CF_3SO_3H (47 μL, 0.53 mmol). The color changed immediately from red to brown. The mixture was stirred for 15 min at room temperature, after which a solution of *p*-cresol (44 mg, 0.41 mmol) in dichloromethane (5 mL) was added. The mixture was stirred for 2 h, and the solvent was removed from the resulting brown solution. Crystallization from dichloromethane/diethyl ether afforded a microcrystalline white solid (**10**). Yield: 100%. Anal. Calcd for $C_{18}H_{23}F_3O_4SRu$: C, 43.81; H, 4.70. Found: C, 43.80; H, 4.69. ^{1}H NMR (Me_2CO-d_6): δ 2.09 (s, 15 H, C_5Me_5), 2.30 (s, 3 H, Me), 5.93 (s, 4 H). ^{13}C NMR (Me_2CO-d_6): 9.47 (q, C_5Me_5), 17.05 (q, C*Me*), 77.24 (d, J = 175.3 Hz, *C*H), 86.6 (d, J = 173.2 Hz, *C*H), 95.12 (s, C_5Me_5), 97.13 (s, *C*Me), 129.92 (s, *C*OH).

(2) $[Cp^*Ru(\eta^6\text{-}4\text{-}MeC_6H_4OMe)]CF_3SO_3$ (11). To a solution of **10** (0.56 mmol) in CH_2Cl_2 was added CH_3I (0.56 mmol, 34 μL), and the solution was stirred for 1 day. After removal of the solvent, the residue was recrystallized from dichloromethane/diethyl ether, affording white microcrystals of the complex. Yield: 80%. Anal. Calcd for $C_{19}H_{25}F_3O_4SRu{\cdot}H_2O$: C, 43.43; H, 5.14. Found: C, 43.68; H, 4.75. ^{1}H NMR (Me_2CO-d_6): 2.13 (s, 15 H, C_5Me_5), 2.32 (s, 3 H, Me), 3.99 (s, 3 H), 6.20 (q, 4 H). ^{13}C NMR (Me_2CO-d_6): δ 9.47 (q, C_5Me_5), 16.95 (q, C*Me*), 5.67 (s, CO*Me*), 76.21 (d, J = 175.3 Hz, *C*H), 87.36 (d, J = 175.1 Hz, *C*H), 95.48 (s, C_5Me_5), 99.60 (s, *C*Me), 126.66 (s, *C*OMe).

(3) $[Cp^*Ru(\eta^6\text{-}3,5\text{-}Me_2C_6H_3OH)]CF_3SO_3$ (12). 3,5-Dimethylphenol was added to a solution of CF_3SO_3H (47 μL, 0.53 mmol) and $[Cp^*RuOMe]_2$ (110 mg, 0.20 mmol) in dichloromethane, and the resulting solution was stirred for 2 h. **12** was obtained as a white solid upon recrystallization from dichloromethane/diethyl ether as before. Yield: 100%. Anal. Calcd for $C_{19}H_{25}F_3O_4SRu$: C, 44.96; H, 4.97. Found: C, 45.26; H, 5.15. ^{1}H NMR (Me_2CO-d_6): 2.03 (s, 15 H, C_5Me_5), 2.31 (s, 6 H, Me), 5.83 (s, 2 H), 5.70 (s, 1 H). ^{13}C NMR (Me_2CO-d_6): 9.31 (q, C_5Me_5), 17.75 (q, C*Me*), 77.85 (d, J = 172.7 Hz, *C*H), 86.6 (d, J = 173.2 Hz, *C*H), 94.26 (s, C_5Me_5), 99.34 (s, *C*Me), 130.64 (s, *C*OH).

(4) $[Cp^*Ru(\eta^6\text{-}3,5\text{-}Me_2C_6H_3OMe)]CF_3SO_3$ (13). 3,5-Dimethylphenol (68 mg, 0.56 mmol) was added to a solution of CF_3SO_3H (57 μL, 0.60 mmol) and $[Cp^*RuOMe]_2$ (150 mg, 0.28 mmol) in dichloromethane (10 mL). The resulting solution was stirred for 2 h, CH_3I (34 μL, 0.56 mmol) was added, and the mixture was stirred for another 2 h. **12** was obtained as a white microcrystalline solid upon recrystallization from dichloromethane/diethyl ether. Yield: 90%. Anal. Calcd for $C_{20}H_{27}F_3O_4SRu \cdot H_2O$: C, 44.52; H, 5.42. Found: C, 44.75; H, 5.66. ^1H NMR (Me_2CO-d_6): 2.08 (s, 15 H, C_5Me_5), 2.40 (s, 6 H, Me), 3.99 (s, 3 H), 5.94 (s, 1 H), 6.32 (s, 2 H). ^{13}C NMR (Me_2CO-d_6): 9.50 (q, C_5Me_5), 17.73 (q, C*Me*), 57.0 (s, CO*Me*), 77.85 (d, *C*H), 87.35 (d, *C*H), 94.57 (s, C_5Me_5), 99.52 (s, *C*Me), 130.00 (s, *C*OMe).

Disordered Guest and Water Molecules. Three-Center and Flip-Flop O-H···O Hydrogen Bonds in Crystalline β-Cyclodextrin Ethanol Octahydrate at T = 295 K: A Neutron and X-ray Diffraction Study†

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Abstract: A single crystal neutron diffraction study of partially deuterated β-cyclodextrin ethanol octahydrate was carried out at T = 295 K, composition $(C_6H_7D_3O_5)_7 \cdot C_2D_5OD \cdot 8D_2O$, space group $P2_1$, cell constants a = 21.125 (2) Å, b = 10.212 (1) Å, c = 15.215 (2) Å and β = 111.47 (1)°; 4138 unique neutron data (λ = 1.3167 Å) with nominal resolution 0.93 Å (2θ ≤ 90°). All H and D atoms were located and the structure was refined to R = 6.6%. In the β-CD molecule, 2-fold orientational disorder is found for two of the seven CH_2(6)–O(6) groups and for 15 of the 21 hydroxyl groups; one hydroxyl group is 3-fold disordered. Five water molecules are located between the β-CD macrocycles; two of them have four partially occupied hydrogen atom sites, two have three hydrogen sites, and only one is ordered. One ethanol and three water molecules are enclosed in the β-CD cavity, the ethanol molecule occupying two and the water molecules occupying four alternative discrete sites. The ethanol hydroxyl orientation and the water orientations are disordered for all these sites. In both positions, the ethanol molecule has a well-defined site for the oxygen atom, which is determined by hydrogen bond formation, while the CH_2–CH_3 group vibrates extensively. The two hydrogen-bonding networks in the cavity were assigned individually for both ethanol sites. Hydrogen bonding in the cavity is geometrically disadvantageous, and thermal parameters are higher than for the rest of the structure, indicating considerable solvent mobility in this region. One water molecule forms a hydrogen bond with a glycosidic O(4) oxygen atom of the cavity wall. Out of the 68 symmetry independent hydrogen bonds, 22 (=32%) are of the three-center and two (=3%) of the four-center type (based on a 2.8 Å-cutoff criterion for $d_{D\cdots O}$), and 44 are engaged in $O-{}^1/_2D\cdots{}^1/_2D-O$ flip-flop type disorder. The latter comprise the seven intramolecular, interglucose O(2)···O(3) interactions with a three-center minor component to the corresponding O(4) atoms. There are minor three-center components O(6)–D···O(5) in four glucoses, and O(5) and O(6) of two glucoses accept a three-center chelated hydrogen bond from a hydroxyl group. In two cases, there are weak minor hydrogen bond components between O(2) and O(3) of the *same* glucose. An X-ray study of a different crystal of the same partially deuterated compound showed a significantly different arrangement of the solvent molecules in the β-CD cavity. This implies that in biological crystal structures even of this moderate size hydrogen bonding networks can be reliably determined only for individual single crystals and may be different in others.

Introduction

The torus-shaped cyclodextrins are a family of cyclic oligosaccharides consisting of six (α-CD), seven (β-CD), eight (γ-CD), or nine (δ-CD) D-glucoses connected by α(1–4) interglucose bonds. They readily form inclusion complexes with guest molecules of suitable size, which are of interest in the study of noncovalent interactions and are used for certain industrial applications.[1-3] Many of the complexes crystallize so well that they can be studied by X-ray and neutron diffraction techniques. As each of the glucoses has three free hydroxyl groups and the crystal structures always contain several hydration water molecules, a large number of O–H···O hydrogen bonds are formed, which are interconnected into complicated three-dimensional networks. The guest molecules enclosed in the cyclodextrin cavities tend to be more or less disordered. In our laboratory we use crystalline cyclodextrin complexes as model systems to study their ordered and disordered hydrogen bonding networks, which are of biological interest.

In the room-temperature crystal structure of α-CD·6H_2O, a well-ordered system of cycles and chains of hydrogen bonds is observed.[4,5] In β-CD·11H_2O the situation is more complex. Neutron diffraction disclosed that at room temperature the 11 water molecules per asymmetric unit are disordered over 16 positions, of which only three are fully occupied.[6,7] Five water molecules and 15 (out of 21) hydroxyl groups of the β-CD molecule display orientational disorder, where the hydrogen (deuterium) atoms are found in partially occupied discrete sites.

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