Activation of Carbon–Sulfur and Carbon–Chlorine Bonds by the Electrophilic Ruthenium Fragment '$Ru(\eta\text{-}C_5Me_5)^+$'

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The '$Ru(\eta\text{-}C_5Me_5)^+$' fragment generated by protonation of $[\{Ru(\eta\text{-}C_5Me_5)(OMe)\}_2]$ by CF_3SO_3H, reacted with cyclohexene sulfide to give $[Ru(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ **1** and H_2S. With 1,4-dithiane no C–S bond activation was observed but instead the successive formation of $[Ru(\eta\text{-}C_5Me_5)(S_2C_4H_8)(CF_3SO_3)]$ **2** and $[Ru(S_2C_4H_8)_3]^{2+}$ **3**, whereas with 1,3-dithiane two compounds resulting from the sequential activation of C–S bonds were isolated as $CF_3SO_3^-$ salts, namely $[\{Ru(\eta\text{-}C_5Me_5)(SMe)(SCH_2CH{=}CH_2)\}_2]^{2+}$ **4** and $[\{Ru[C_5Me_4CH_2S(CH_2)_3SMe]\}_2]^{2+}$ **5**. The fragment also reacted with neat dichloromethane to give two trinuclear clusters: $[\{Ru(\eta\text{-}C_5Me_5)\}_3(\mu\text{-}Cl)_3(\mu_3\text{-}CH)]^+$ **6** and $[\{Ru(C_5Me_5)\}_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(\mu_3\text{-}CH)]^{2+}$ **7** in 60 and 30% yield respectively. Its reaction with chlorocyclohexane, 1,2-dichlorocyclohexane and 1,2,3,4,5,6-hexachlorocyclohexane (lindane) yielded **1** and various amounts of H_2 and HCl. In the case of lindane the conversion was only 30% and yielded a 9:1 mixture of **1** and $[Ru(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5Cl)]^+$ **9**. Finally the reaction of C–Cl *versus* C–O bond activation was compared using 2-chlorocyclohexanone, 2-chlorocyclohexanol and 2,2,6,6-tetrachlorocyclohexanol. It was found that in all cases the C–Cl activation was easier. The first reaction yielded **1**, the second the new trinuclear cluster $[\{Ru(C_5Me_5)\}_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(\mu_3\text{-}CCl)]^{2+}$ **11** similar to **7**. The latter reaction depended upon the reaction conditions, but in tetrahydrofuran at 80 °C, an 80% conversion was observed yielding a 1:7:<1 mixture of **1**, $[Ru(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5OH)]^+$ **10** and $[Ru(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5Cl)]^+$ **9** thus demonstrating a high selectivity for C–Cl activation in the presence of C–O bonds.

Much interest has been devoted during the past decade to the activation of carbon–hydrogen and carbon–carbon bonds.[1] Thus selective activation of alkanes is still a challenging problem as far as their use as new intermediates for the chemical industry is concerned. Many systems have now been discovered which allow the activation of carbon–hydrogen bonds using either nucleophilic or electrophilic transition-metal complexes. The activation of carbon–carbon bonds remains however much less documented.[2]

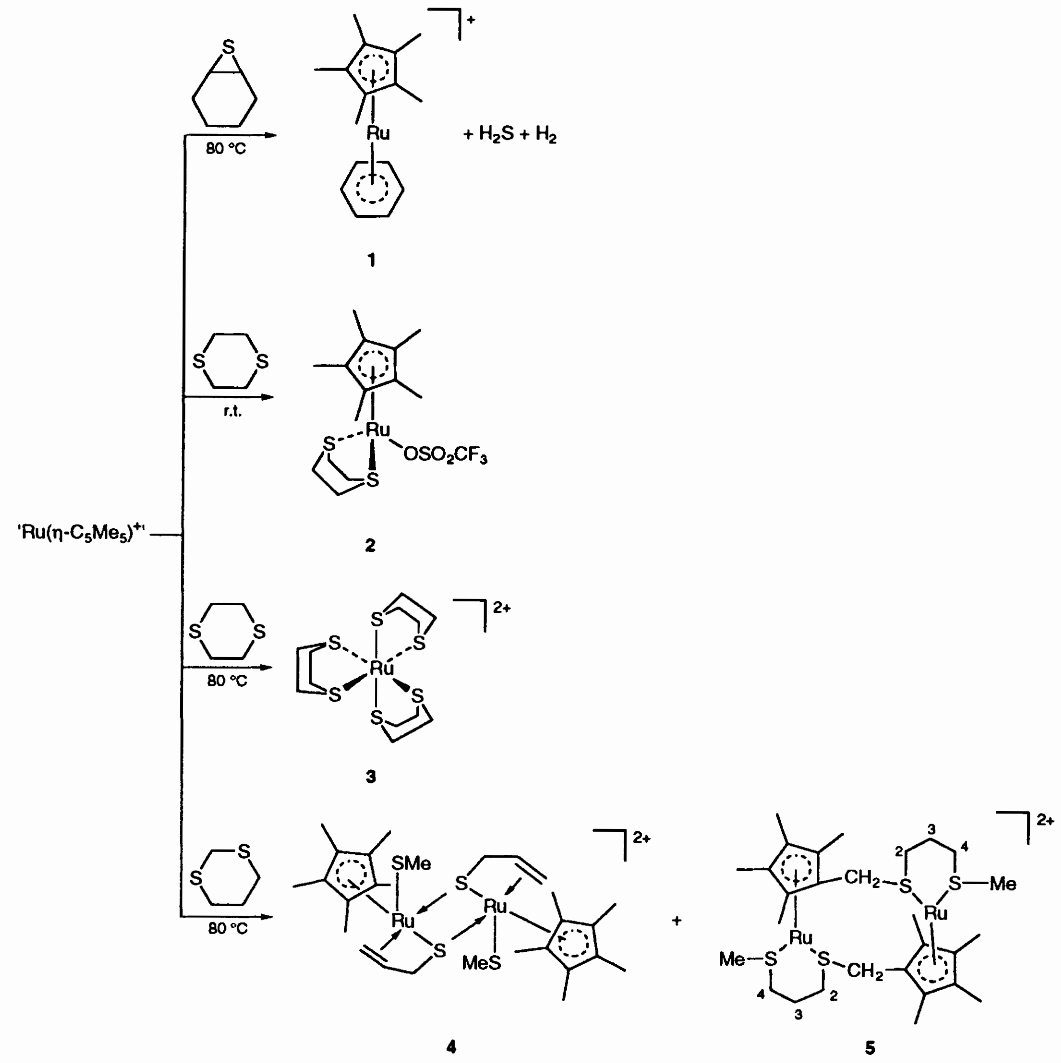
The '$Ru(\eta\text{-}C_5Me_5)^+$' fragment, prepared in our hands by protonation of $[\{Ru(\eta\text{-}C_5Me_5)(OMe)\}_2]$ by trifluoromethanesulfonic acid, shows a very high reactivity towards hydrocarbons. In particular, it is possible to aromatize cyclic C_6 hydrocarbons through C–H, C–O or even C–C bond activation.[3] This property has led to very selective aromatization of the A or B ring of steroids[4] as well as to catalytic isomerization and oligomerization of *tert*-butylethylene through methyl migration and to a novel 'cracking' reaction.[5] The activation of C–O bonds by '$Ru(\eta\text{-}C_5Me_5)^+$' was found to be particularly easy and shown to occur at room temperature. Since this process is usually difficult in the presence of transition metals, we were led to consider the activation of other polar carbon heteroatom bonds. Although the oxidative addition of carbon–halogen bonds in nucleophilic transition-metal complexes has been studied extensively over the past thirty years, in particular Vaska's complex $[IrCl(CO)(PPh_3)_2]$,[6] much less attention has been given to the activation of carbon–chlorine bonds by electrophilic systems. This problem is, however, important in view of the search for a dechlorination catalyst related to environmental problems.[7] Furthermore the activation of carbon–sulfur bonds is presently an area of intensive activity related to the search for a possible model for the hydrodesulfurization process.[8] Hence, this process is of very high commercial importance but little is still known of its mechanism. Several groups, in particular that of Angelici, have studied model desulfurization reactions starting with reasonable models of oil contaminants such as thiophene and benzothiophene.[9] Several studies have now accounted for ring opening and sulfur elimination from thiophenes as well as for the H/D exchange reactions observed on the commercial catalysts.[9–11] However '$Ru(\eta\text{-}C_5Me_5)^+$' was shown to co-ordinate to the π system of thiophene or to the benzene ring of benzothiophene without further reactions in the absence of added bases.[12] We have therefore examined the reactions of '$Ru(\eta\text{-}C_5Me_5)^+$' with saturated systems which could be related to an alternative model of hydrodesulfurization involving first hydrogenation and then desulfurization.

Herein we report the reactions of '$Ru(\eta\text{-}C_5Me_5)^+$' with saturated hydrocarbons containing chlorine or sulfur. Preliminary results on carbon–chlorine activation have been reported.[13]

Results and Discussion

Reactions of '$Ru(\eta\text{-}C_5Me_5)^+$' *with Sulfur-containing Molecules.*—In view of the known reactivity of '$Ru(\eta\text{-}C_5Me_5)^+$', we considered cyclic compounds in which the sulfur atom is incorporated in the ring or α to a C_6 ring. Thus we studied reactions with cyclohexene sulfide (7-thiabicyclo[4.1.0]heptane), 1,3- or 1,4-dithiane, cyclohexanethiol and thiacyclohexane. The two last reactions did not lead to any conclusive results. All the other reactions are shown in Scheme 1.

With cyclohexene sulfide. The overnight reaction of '$Ru(\eta\text{-}C_5Me_5)^+$' with cyclohexene sulfide at 80 °C in CH_2Cl_2 leads to complete conversion of the hydrocarbon. A complex mixture is formed in which the known $[Ru(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ **1** as its $CF_3SO_3^-$ salt was identified and produced in 30% yield. It is interesting that this reaction is accompanied by the evolution of dihydrogen and hydrogen sulfide in the gas phase as detected by GLC. To the best of our knowledge this is the first example of such H_2S evolution upon desulfurization. The other components of the mixture could not be separated.



Scheme 1 Reactions of 'Ru(η-C_5Me_5)$^+$' towards sulfur-containing molecules; r.t. = room temperature

With 1,4-*dithiane*. Reactions with dithianes, although not directly related to the hydrodesulfurization process are much more interesting from the fundamental point of view. Hence, the reaction of 'Ru(η-C_5Me_5)$^+$' with 1,4-dithiane at room temperature in CH_2Cl_2 leads to the clean formation of a new complex **2** isolated as an off-white powder in 40% yield. Its structure, [Ru(η-C_5Me_5)($S_2C_4H_8$)(CF_3SO_3)], is based on ^1H, ^{13}C NMR spectra, microanalysis and mass spectroscopic data. The ^1H NMR spectrum of **2** in [$^2H_6$]acetone shows the C_5Me_5 methyl groups at δ 1.94 and the methylene protons of the 1,4-dithiane ligand as a multiplet centred at δ 3. In $CDCl_3$, several signals corresponding to C_5Me_5 are observed as well as a series of multiplets between δ 3 and 3.8 for the methylene protons of 1,4-dithiane. The ^{13}C NMR spectrum in $CDCl_3$ also shows the presence of at least four different compounds with singlets centred at δ 10, 97 and 36 respectively for $C_5\mathit{Me}_5$, C_5Me_5 and the methylene protons of 1,4-dithiane. Interestingly, the CF_3SO_3 carbon which usually gives rise to a sharp quartet shows two sets of signals near δ 120 and 108. These observations can be attributed to an equilibrium between several compounds containing or not co-ordinated $CF_3SO_3^-$, $CDCl_3$, and different conformers. In acetone, only [Ru(η-C_5Me_5)($S_2C_4H_8$)(CF_3SO_3)] is found and the mass spectrum confirms the co-ordination of $CF_3SO_3^-$. Using the desorption chemical ionization (DCI) technique (carrier gas NH_3) we observed a peak at *m*/*z* 524 corresponding to [Ru(C_5Me_5)($S_2C_4H_8$)(CF_3SO_3)(NH_4)]$^+$ (intensity 7.6%) and its fragmentation into [Ru(C_5Me_5)($S_2C_4H_8$)(NH_3)]$^+$ at *m*/*z* 374 (18.4%) and [Ru(C_5Me_5)($S_2C_4H_8$)]$^+$ at *m*/*z* 357 (21.0%). All peaks are calculated for ^{102}Ru and exhibit the correct isotopic pattern of ruthenium.

When 'Ru(η-C_5Me_5)$^+$' was treated with an excess of 1,4-dithiane, yellow crystals were isolated after recrystallisation from acetone–diethyl ether. However the spectroscopic data only showed the presence of **2** and free 1,4-dithiane in solution. From microanalytical data and integration ratios in ^1H NMR, we conclude that the excess 1,4-dithiane is not co-ordinated even in chloroform and that a 0.5–0.7 equivalent of free 1,4-dithiane is incorporated in the crystal lattice.

When a 1 : 1 reaction mixture of 'Ru(η-C_5Me_5)$^+$' and 1,4-dithiane in CH_2Cl_2 is heated at 80 °C for 20 h, a white powder precipitates in *ca.* 30% yield. The complex analyses as the $CF_3SO_3^-$ salt of [Ru($S_2C_4H_8$)$_3$]$^{2+}$ **3** and shows very simple spectroscopic properties: two multiplets centred at δ 3.30 and 3.05 in the ^1H NMR and two triplets at δ 35.3 (J_{CH} 150) and 37.9 (J_{CH} 150 Hz) in the ^{13}C NMR spectra. It is clear from these data that no activation of a C–S bond occurred in this system and that only the C_5Me_5 ligand has been replaced. The fate of the remaining ruthenium was not elucidated. Presumably **3** shows an octahedral RuS_6 structure found previously in [Ru([9]aneS_3)$_2$] ([9]aneS_3 = 1,4,7-triazacyclononane)[14] to be particularly stable.

With 1,3-*dithiane*. The reaction of 'Ru(η-C_5Me_5)$^+$' with 1 equivalent of 1,3-dithiane at 80 °C for 20 h yields an orange precipitate **4** and a brown solution. Occasionally **4** does not precipitate, and then it is necessary to evaporate the reaction mixture to dryness and redissolve it in acetone whereupon **4** will separate from the solution. In both cases, the remaining oily brown solution is evaporated to dryness and treated with diethyl ether to give a brown powder **5**. The yield of **4** is consistently *ca.* 30–40% (see Experimental section) whatever the method of preparation, and the yield of **5** near 20%. Once isolated, **4** is insoluble in common organic solvents [CH_2Cl_2, $CHCl_3$, benzene, tetrahydrofuran (thf), methanol, ethanol], slightly soluble in acetone and very soluble in dimethyl sulfoxide (dmso). We checked that the ^1H NMR spectra were similar whether recorded in [$^2H_6$]acetone or [$^2H_6$]dmso and therefore that no reaction had occurred between **4** and dmso. The ^1H NMR spectrum of **4** in dmso shows five signals: a complex multiplet centred at δ 4.11 (3 H), a broad doublet of doublets at δ 3.63 (1 H, J_{HH} 12, 3 Hz), a singlet at δ 3.46 covering another signal as observed by decoupling experiments (total 4 H), and a singlet for the C_5Me_5 ligand at δ 1.75 (15 H). The signal at δ 3.63 is linked to that at δ 4.11 by a coupling constant of 3 Hz and to that near δ 3.4 by one of 12 Hz. The ^{13}C NMR spectrum is very simple exhibiting peaks at δ 16.54 (q, J_{CH} 143), 89.0 (d, J_{CH} 167), 50.3 (t, J_{CH} 145) and 44.4 (t, J_{CH} 131 Hz) in addition to the resonances of the C_5Me_5 ligand found at δ 8.65 (q, J_{CH} 129 Hz) and 102.2 (s). The proposed structure for **4** shown in Scheme 1 fits these data. Thus there would be a splitting of the 1,3-dithiane into a SMe and a SCH_2CHCH_2 group. The former would appear at δ 3.46 in the ^1H NMR and δ 16.54 in the ^{13}C NMR spectra. In the latter group the methylene protons α to sulfur would resonate at δ 3.63 and 3.4 and the carbon at δ 44.4 whereas the olefinic protons would all be found near δ 4.11 and the corresponding carbons at δ 89.0 and 50.3. However several other structures could fit these data and in particular those involving bridging methylthio or even bridging sulfide ligands. Mass spectrometry using the DCI technique was undertaken to distinguish between these possibilities. The most intense peaks correspond to the monomer $[Ru(\eta\text{-}C_5Me_5)(SCH_2CHCH_2)SMe]^+$ (intensity 37.4%) at *m/z* 357 and to the loss of HSMe from this monomer at *m/z* 309 ($[C_5Me_4CH_2RuSCH_2CHCH_2]^+$) (13.4%). Peaks corresponding to the presence of two rutheniums were observed: $[Ru_2(C_5Me_5)_2(SCH_2CHCH_2)_2SMe]^+$ (*m/z* 667, 1.2%), $[(C_5Me_5)(C_5Me_4CH_2)(Ru_2)(SCH_2CHCH_2)_2]^+$ (*m/z* 619, 2.5%) and $[Ru_2(C_5Me_5)_2(SCH_2CHCH_2)S]^+$ (*m/z* 578, 1.3%). These peaks correspond respectively to the loss of SMe and further loss of HSMe from the non-detected parent ion. Since the structure remains dinuclear upon losing the methylthio groups, the proposed structure shown in Scheme 1, although surprising, is the most likely. The NMR spectra clearly show that the $S\text{–}CH_2$ bond is not broken.

Compound **5**, which could be an intermediate in the formation of **4**, shows a microanalysis similar to **4** implying that only a rearrangement occurs. The most salient feature of the ^1H NMR spectrum is the presence of an AB-type spectrum at δ 5.1 and 4.8 (J_{AB} 13 Hz) similar to that obtained by Maitlis and co-workers[15] from a ruthenium derivative containing a $C_5Me_4(CH_2Cl)$ ligand.[15] The other resonances attributed to the methyl group of the C_5Me_5 ligand appear as overlapping multiplets near δ 1.8 instead of the usual sharp singlet. A singlet is observed for a sulfur-bound methyl group at δ 3.40 and three multiplets at δ 3.9, 3.1 and 2.5 for the methylene protons of the C_3 chain of the activated dithiane ligand. They are attributed to methylene groups 2, 4 and 3 respectively (see Scheme 1). The ^{13}C NMR spectrum shows four triplets for the four methylene carbons at δ 22.2, 27.0, 38.6 and 40.1. The two latter peaks correspond to methylene groups of the former dithiane ring linked directly to sulfur. The C_5 ring appears as several overlapping peaks near δ 9.2 whereas the corresponding quaternary carbons resonate near δ 100. A $^1H\text{–}^1H$ COSY experiment shows the expected correlations between the methylene groups and an extra cross peak between the methylene group attached to the C_5 ring and methylene 2 which could reveal either a coupling through sulfur or through space since a molecular model shows a close contact between the protons of the two groups in a dinuclear system. Finally the mass spectrum only shows mononuclear fragments corresponding to the monomer $[C_5Me_4CH_2RuCH_3S(CH_2)_3S]^+$ (25.3%) at *m/z* 357, loss of a methylene group $[C_5Me_5RuS(CH_2)_3S]^+$ (16.2%) at *m/z* 343, further loss of a methyl group $[C_5Me_4HRuS(CH_2)_3S]^+$ (81.2%) at *m/z* 329 and addition of a methylene group to the monomer $[C_5Me_4CH_2RuCH_3S(CH_2)_3SCH_2]^+$ (100%) at *m/z* 371. The presence of the last peak with high intensity is in agreement with a dinuclear structure.

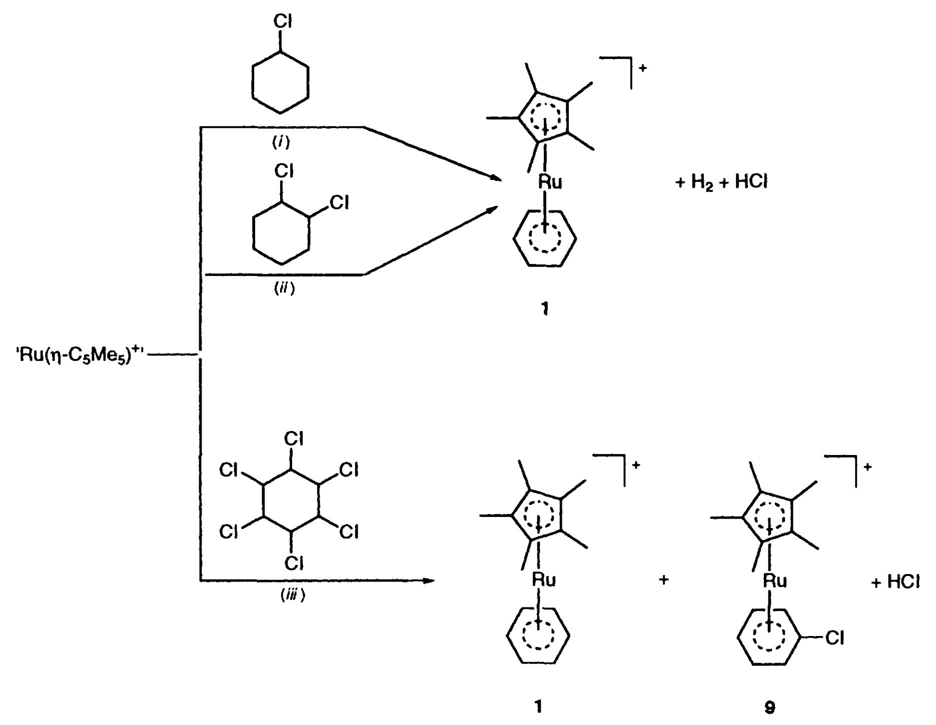
Thus, the reaction of '$Ru(\eta\text{-}C_5Me_5)^+$' with 1,3-dithiane yields two isolable compounds in reasonable yields. Both compounds result from the activation of C–S bonds. In **5**, the $(CH_2)_3S_2$ fragment is not broken but a proton transfer has occurred between a methyl group of C_5Me_5 and a methylene group α to sulfur. Further activation of a C–S bond leads to **4** which contains an allyl sulfido group. It is not clear whether **5** is an intermediate in the formation of **4**. Two arguments support this proposal: (*i*) **5** could not be isolated after prolonged heating of the reaction solution; (*ii*) two-dimensional NMR shows in **5** a close contact between the methylene group on the C_5Me_5 ring and a methylene group of the C_3 moiety arising from dithiane. This could favour a proton transfer upon C–S bond breaking and formation of **4**. However it appears that the processes are not entirely selective and therefore it is difficult to make conclusions. Nevertheless, we have shown that C–S bond activation is easier with 1,3-dithiane as compared to 1,4-dithiane.

Activation of Carbon–Chlorine Bonds.—Ruthenium complexes containing a C_5R_5 ligand have been previously shown to undergo activation of carbon–halogen bonds. For example Singleton and co-workers,[16] showed that the complex $[Ru(\eta\text{-}C_5H_5)(1,5\text{-}C_8H_{12})Br]$ was able to dehydrobromate bromocyclohexene into benzene. The tetramer $[\{Ru(\eta\text{-}C_5Me_5)Cl\}_4]$ reacts with allyl chloride[17] to yield the ruthenium(IV) allyl dichloride complex $[Ru(\eta\text{-}C_5Me_5)(\eta^3\text{-}C_3H_5)Cl_2]$ whereas μ-methylene derivatives are found upon reaction of $[Ru_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)_2]$ with MeI or CH_2Cl_2.[18]

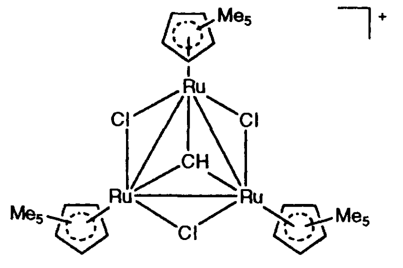
Reactions of '$Ru(\eta\text{-}C_5Me_5)^+$'.—*With* CH_2Cl_2. During activation reactions, in particular of C–C bonds carried out in CH_2Cl_2, we observed the formation of an intense green colour in the reaction solution.[3] The same colour appears if '$Ru(\eta\text{-}C_5Me_5)^+$' is refluxed in CH_2Cl_2 in the absence of any additive. Upon crystallization of the reaction solution, three compounds were obtained, **6**–**8**, in respectively *ca.* 60, 30 and 10% yield.

The first is a trinuclear ruthenium cluster $[\{Ru(\eta\text{-}C_5Me_5)\}_3(\mu\text{-}Cl)_3(\mu_3\text{-}CH)]^+$ **6** with a μ_3-methylidyne group characterized by a signal at δ 19.78 in the ^1H NMR spectrum. Complex **6** as its BF_4^- salt has previously been obtained by Suzuki and co-workers[19] from the reaction of $[\{Ru(\eta\text{-}C_5Me_5)Cl_2\}_n]$ with $AgBF_4$ in the presence of acetaldehyde (the yield was not mentioned) or from treatment with $CHCl_3$ of the similar cluster $[\{Ru(\eta\text{-}C_5Me_5)\}_3(\mu\text{-}H)(\mu\text{-}Cl)_2(\mu_3\text{-}CH)]BF_4$ prepared by action of $AgBF_4$ on $[\{Ru(\mu\text{-}C_5Me_5)Cl_2\}_n]$ in the presence of ethanol in 40% yield.

The second compound, **7**, was identified by spectroscopic methods as the $CF_3SO_3^-$ salt of the cluster $[\{Ru(\eta\text{-}C_5Me_5)\}_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(\mu_3\text{-}CH)]^{2+}$. The bridging carbonyl ligand is characterized by a band at 1847 cm^{-1} in its IR spectrum and by a signal at δ 206.2 in its ^{13}C NMR spectrum. The methylidyne carbon is observed at δ 340.6 (J_{CH} 177 Hz); the corresponding proton resonates at δ 16.37 in the ^1H NMR spectrum. Complex **7** is similar to **6** except for the substitution of a chloride by a carbonyl group. The carbonyl group probably originates from the methanol molecule produced upon protonation of $[\{Ru(\eta\text{-}C_5Me_5)(OMe)\}_2]$ with CF_3SO_3H. Finally another green crystalline material, **8**, was obtained in low yield (*ca.* 10%). It is probably similar to **6** and **7** but is paramagnetic and was not characterized.



Scheme 2 Activation of C–Cl bonds by '$Ru(\eta\text{-}C_5Me_5)^+$'; (*i*) r.t., 60% conversion; (*ii*) 80 °C, 90% conversion; (*iii*) 100 °C, 30% conversion



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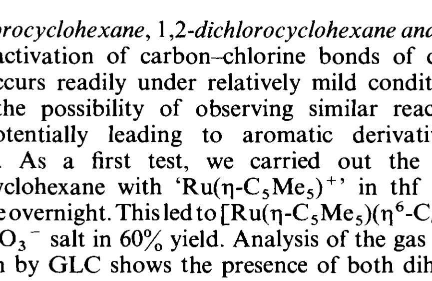

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With chlorocyclohexane, 1,2-*dichlorocyclohexane and lindane*. Since the activation of carbon–chlorine bonds of dichloromethane occurs readily under relatively mild conditions, we examined the possibility of observing similar reactions in systems potentially leading to aromatic derivatives (see Scheme 2). As a first test, we carried out the reaction of chlorocyclohexane with '$Ru(\eta\text{-}C_5Me_5)^+$' in thf at room temperature overnight. This led to $[Ru(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ **1** as its $CF_3SO_3^-$ salt in 60% yield. Analysis of the gas phase of the reaction by GLC shows the presence of both dihydrogen and hydrochloric acid. Heating the reaction mixture to 80 °C does not lead to any better yield of **1**. This is probably due to the competitive reaction of thf polymerization previously demonstrated to occur in the presence of '$Ru(\eta\text{-}C_5Me_5)^+$'.

If 1,2-dichlorocyclohexane is used, reaction proceeds very slowly at room temperature but at 80 °C the reaction selectively produces **1** in 90% yield. This difference of reactivity is surprising but could be explained by the initial chelation of 1,2-dichlorocyclohexane to '$Ru(\eta\text{-}C_5Me_5)^+$'. Co-ordination of carbon–halogen bonds to a transition metal has a few precedents in cationic iridium or ruthenium compounds.[20] This type of chelation (see Fig. 1) could explain why the reaction is slow at room temperature and why a rapid and selective dehydrohalogenation occurs at high temperature.

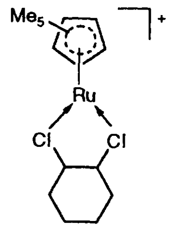
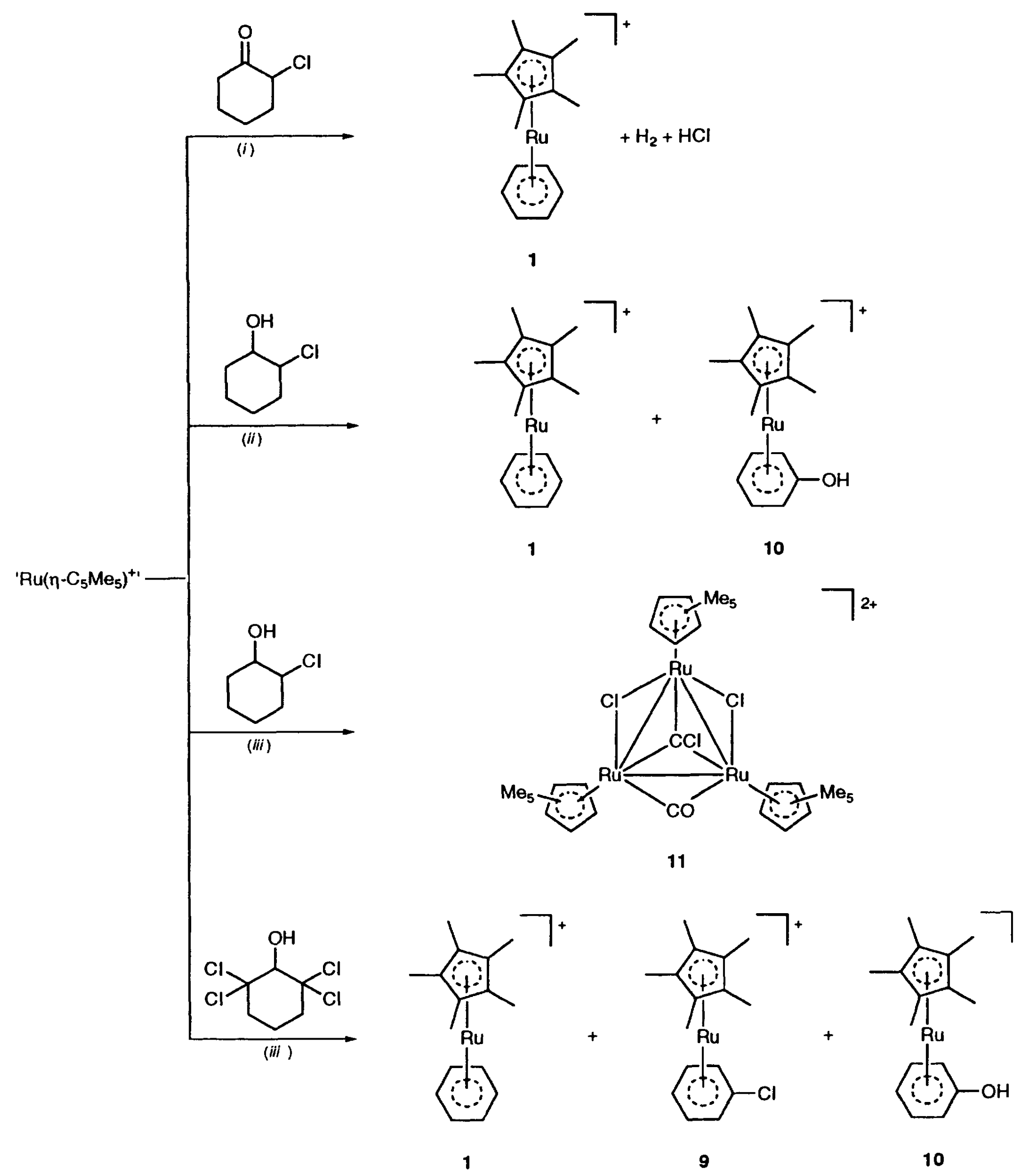


Fig. 1 Proposed structure for an intermediate during the reaction of '$Ru(\eta\text{-}C_5Me_5)^+$' with 1,2-dichlorocyclohexane

The dehydrohalogenation reaction of both chloro- and 1,2-dichloro-cyclohexane has been attempted in the presence of dihydrogen since it could lead to a catalytic hydrodehalogenation of hydrocarbons. However, we observed little or no change in the reactions which were only stoichiometric and led to **1** in 50 and 90% yields respectively. Analysis of the reaction mixture by GLC did not show any evidence for the presence of cyclohexane.

In order to explore the potential of this carbon–chlorine bond activation reaction, we extended it to lindane. Lindane (1,2,3,4,5,6-hexachlorocyclohexane) is an extremely stable molecule which is damaging the environment. In thf at 100 °C a conversion of 30% of lindane is observed to give a 9 : 1 mixture of **1** and $[Ru(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5Cl)]^+$ **9**, which were identified by comparison with authentic samples. An authentic sample of **9** was synthesised by treating '$Ru(\eta\text{-}C_5Me_5)^+$' with chlorobenzene (see Experimental section).

With 2-*chlorocyclohexanone*, 2-*chlorocyclohexanol and* 2,2,6,6-*tetrachlorocyclohexanol*. Finally it was of interest to compare the reactivity of C–Cl *vs*. C–O bonds towards '$Ru(\eta\text{-}C_5Me_5)^+$'. With 2-chlorocyclohexanone the reaction proceeds rapidly at room temperature to produce **1** in *ca*. 90% yield. However the conversion of 2-chlorocyclohexanol is only 10%,



Scheme 3 Competitive activation of C–Cl *vs.* C–O bonds by 'Ru(η-C_5Me_5)$^+$'; (*i*) r.t., CH_2Cl_2, 90% conversion; (*ii*) r.t., thf, 10% conversion; (*iii*) 80 °C, thf, 80% conversion

at room temperature, giving a 10:1 mixture of [Ru(η-C_5Me_5)(η^6-C_6H_5OH)]$^+$ **10** and **1**. Heating the reaction solution at 80 °C leads to thf polymerisation and the formation of a new trinuclear cluster [{Ru(η-C_5Me_5)}$_3$(μ-Cl)$_2$(μ-CO)(μ_3-CCl)]$^{2+}$ **11** in 80% yield as a green crystalline material. The cluster shows properties similar to **7**. For example, the bridging carbonyl ligand is identified by an IR band at 1844 cm^{-1} and a signal at δ 206.3 in the ^{13}C NMR spectrum, whereas two sets of signals are observed for the C_5Me_5 group in the ^{13}C NMR spectrum at δ 10.75 and 10.00 (C_5*Me*$_5$) and 110.8 (br) (*C*$_5$Me$_5$). In the ^1H NMR spectrum two singlets are observed at δ 2.09 and 2.08 in a 2:1 ratio. The difference between **7** and **11** is the absence of the methylidyne proton in the ^1H NMR spectrum. Microanalytical data suggest the presence of a chlorocarbyne ligand. The ^{13}C resonance for the μ_3 bridging group could be shifted considerably and show a large relaxation time which could explain, together with the low solubility of **11** the lack of its observation. We therefore propose the structure shown in Scheme 3 for this cluster. The formation of **11** from the reaction of 'Ru(η-C_5Me_5)$^+$' with 2-chlorocyclohexanol is astonishing, especially since the yield of the reaction is very good. It is clear that C–Cl activation occurs first, perhaps to give a ruthenium-(IV) hydrido chloride derivative which would then rearrange. We could not however obtain any informative data from monitoring the reaction by ^1H NMR spectroscopy.

The reaction of 'Ru(η-C_5Me_5)$^+$' in thf with 2,2,6,6-tetrachlorocyclohexanol proceeds at 80 °C to give a mixture of three compounds **1**, **9** and **10** in a 1:7: < 1 ratio with an overall yield of 80%. In CH_2Cl_2 the overall yield for the reaction is only 30% and the selectivity for **1**, **9** and **10** 1:2:1. The same reaction carried out in the presence of dihydrogen gives the same yield but with a selectivity of 3:1:3.

These experiments demonstrate that carbon–chlorine bond activation is easier than carbon–oxygen activation. As observed previously, a cyclic ketone is much more easily dehydrated than a cyclic alcohol. It is however remarkable that in thf we can selectively remove all four chlorine atoms of 2,2,6,6-tetrachlorocyclohexanol.

Conclusion

This work has shown that the Lewis acidic fragment 'Ru(η-C_5Me_5)$^+$' is able to undergo C–Cl and C–S activation reactions. Whereas the carbon–chlorine bond activation is easy and selective, the reactions of saturated cyclic sulfur derivatives are difficult. It was interesting to observe the reaction with cyclohexene sulfide which led to benzene and the evolution of H_2S. Unfortunately this reaction was unique and a similar attempt with cyclohexanethiol led to intractable mixtures. Reactions with tetrahydrothiophene and thiacyclohexane did not lead to any activation reaction. The selectivity of activation of the carbon–chlorine bond even in the presence of carbon–oxygen bonds is somewhat surprising and is probably related to the initial co-ordination of the chloride ligand on 'Ru(η-C_5Me_5)$^+$'. The reaction with 1,2-dichlorocyclohexane which proceeds slowly at room temperature and is selective at 80 °C could be due to this co-ordination. Unlike in our previous studies on C–H, C–O and C–C bond activation, it was impossible in this case to gain mechanistic information upon monitoring the activation reactions by ^1H NMR spectroscopy. We have therefore no real mechanism to propose for these reactions except similar ones to those previously reported for C–O bond activation.[3]

This work terminates our investigation of the potential of 'Ru(η-C_5Me_5)$^+$' to break carbon–carbon, carbon–hydrogen or carbon–heteroatom bonds. We have previously shown that this approach could lead to selective synthetic applications such as in steroid chemistry. We intend to look for new applications of these processes.

Experimental

All operations were performed under argon using standard Schlenk-tube techniques. Microanalyses were performed by the Centre de Microanalyse du CNRS or in our laboratory. Mass spectrometry was performed by Miss Richelme at the Université Paul Sabatier using the method of desorption chemical ionisation (DCI) of the samples by NH_3 with a NERMAG R10-10 apparatus; the samples were introduced into the mass spectrometer by a direct insertion system. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 or WM250 spectrometer. Activation experiments were carried out in closed Fischer-Porter bottles equipped with Swagelok fittings that can connect directly to the injection valve of an IGC 16 Intersmat gas chromatography system. Identification of H_2 was performed on a $\frac{1}{8}$ inch column: molecular sieve 5 Å (2 m); temperature 80 °C; carrier gas He, 20 cm^3 min^{-1}; thermal conductivity detector; sample loop 0.3 cm^3. For HCl and H_2S detection, Poropack Q and Chromosorb T columns were used respectively. The spectroscopic yields of reactions were determined by integration in both GC and ^1H NMR spectroscopy.

Activation Reactions.—A typical activation reaction was carried out using the following procedure. To a solution of 'Ru(η-C_5Me_5)' prepared from [{Ru(η-C_5Me_5)(OMe)}$_2$] (157 mg, 0.29 mmol) and CF_3SO_3H (70 μl, 0.25 mmol) in 10 cm^3 solvent (CH_2Cl_2 or thf) was added 1 equivalent of the substrate. The solution was then transferred to a Fischer-Porter type bottle and heated for 18 h, generally at 80 °C unless otherwise stated. The solution was then cooled to room temperature and the gas phase (in certain cases the liquid phase) analysed by chromatography. The solution was then transferred back to a Schlenk tube, evaporated to dryness and analysed by ^1H and ^{13}C NMR spectroscopy. This procedure was used for the reactions with cyclohexene sulfide, chlorocyclohexane, 1,2-dichlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 2-chlorocyclohexanone and 2,2,6,6-tetrachlorocyclohexanol. In the other cases, the products were isolated.

Reactions of 'Ru(η-C_5Me_5)$^+$'.—*With* 1,4-*dithiane*. (*a*) *At room temperature*. To a solution of 'Ru(η-C_5Me_5)$^+$' (0.58 mmol) in CH_2Cl_2 (10 cm^3) was added 1,4-dithiane (70 mg, 0.58 mmol). The reaction mixture was stirred at room temperature for 48 h. After evaporation to dryness, the residue was washed three times with distilled water (5 cm^3) and three times with diethyl ether (5 cm^3) yielding [Ru(η-C_5Me_5)($S_2C_4H_8$)(CF_3SO_3)] as a beige solid in 40% yield (Found: C, 35.70; H, 4.95; S, 19.45. Calc. for $C_{15}H_{23}F_3O_3RuS_3$: C, 35.65; H, 4.55; S, 19.00%).

(*b*) *At* 80 °C. To a solution of 'Ru(η-C_5Me_5)' (0.82 mmol) in CH_2Cl_2 (10 cm^3) was added 1 equivalent of 1,4-dithiane (99 mg, 0.82 mmol). The reaction mixture was heated at 80 °C for 20 h during which [Ru($S_2C_4H_8$)$_3$][CF_3SO_3]$_2$ precipitated as a white solid. It was filtered off, washed three times with diethyl ether (5 cm^3) and dried *in vacuo*. Yield 30% (Found: C, 22.05; H, 3.15; S, 32.60. Calc. for $C_{14}H_{24}F_6O_6RuS_8$: C, 22.15; H, 3.15; S, 33.70%).

With 1,3-*dithiane*. To a solution of 'Ru(η-C_5Me_5)$^+$' (0.58 mmol) in CH_2Cl_2 (10 cm^3) was added 1,3-dithiane (70 mg, 0.58 mmol). The reaction mixture was heated at 80 °C for 20 h during which an orange precipitate formed together with a brown solution. After filtration, the orange powder was washed with diethyl ether (15 cm^3) and dried *in vacuo* affording [{Ru(η-C_5Me_5)(SMe)($SCH_2CH{=}CH_2$)}$_2$][CF_3SO_3]$_2$. Yield 30% (Found: C, 35.55; H, 4.55; S, 18.80. Calc. for $C_{15}H_{23}F_3O_3RuS_3$: C, 35.65; H, 4.55; S, 19.00%).

The brown solution was evaporated to dryness and treated with diethyl ether (15 cm^3). A brown powder identified as [{Ru[$C_5Me_4CH_2S(CH_2)_3SMe$]}$_2$][CF_3SO_3]$_2$ was recovered in 20% yield (Found: C, 35.50; H, 4.45. Calc. for $C_{15}H_{23}F_3O_3RuS_3$: C, 35.65; H, 4.55%).

With CH_2Cl_2. A solution of 'Ru(η-C_5Me_5)$^+$' (0.58 mmol) in CH_2Cl_2 (10 cm^3) was heated at 80 °C for 5 h during which it turned deep green. After cooling at room temperature the insoluble green material was filtered off and redissolved in ethanol. The solution was left at room temperature affording green microcrystals of [{Ru(η-C_5Me_5)}$_3$(μ-Cl)$_3$($μ_3$-CH)][CF_3SO_3] in 60% yield (Found: C, 39.55; H, 4.45. Calc. for $C_{32}H_{46}Cl_3F_3O_3Ru_3S$: C, 39.30; H, 4.75%).

After filtration of **6**, the remaining solution was cooled at 0 °C. Green microcrystals of [{Ru(η-C_5Me_5)}$_3$(μ-Cl)$_2$(μ-CO)($μ_3$-CH)][CF_3SO_3]$_2$ deposited in 30% yield (Found: C, 36.45; H, 4.45. Calc. for $C_{34}H_{46}Cl_2F_6Ru_3S_2$: C, 36.50; H, 4.15%).

With 2-*chlorocyclohexanol*. To a solution of 'Ru(η-C_5Me_5)$^+$' (0.49 mmol) in thf (10 cm^3) was added 2-chlorocyclohexanol (58 μl, 0.49 mmol). The reaction mixture was heated at 80 °C for 20 h during which the solution turned deep green. The solution was then evaporated to dryness and the residue recrystallized from CH_2Cl_2–Et_2O affording a green microcrystalline solid characterized as [{Ru(η-C_5Me_5)}$_3$(μ-Cl)$_2$(μ-CO)($μ_3$-CCl)][CF_3SO_3]$_2$. Yield *ca*. 80% (Found: C, 35.40; H, 4.05. Calc. for $C_{34}H_{45}Cl_3F_6O_7Ru_3S_2$: C, 35.40; H, 3.95%).

Preparation of an Authentic Sample of [Ru(η-C_5Me_5)($η^6$-C_6H_5Cl)][CF_3SO_3].—To a solution of 'Ru(η-C_5Me_5)$^+$' (0.58 mmol) in CH_2Cl_2 (20 cm^3) was added 1 equivalent chlorobenzene. After 2 h at room temperature the solution was concentrated to *ca*. 5 cm^3. Addition of diethyl ether (5 cm^3) led to the precipitation of a white powder that after washing with H_2O was obtained in 85% yield and analysed as [Ru(η-C_5Me_5)($η^6$-C_6H_5Cl)][CF_3SO_3]·2H_2O (Found: C, 38.50; H, 4.10. Calc. for $C_{17}H_{24}ClF_3O_5RuS$: C, 38.25; H, 4.50%).

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