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Preliminary communication

Selective activation of carbon-chlorine bonds by the electrophilic fragment "Cp^*Ru^+"

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Abstract

The "Cp^*Ru^+" fragment (**1**) reacts with cyclic chlorinated hydrocarbons $C_6H_{11}Cl$, 1,2-$C_6H_{10}Cl_2$, α-$C_6H_6Cl_6$ and 1,2-$C_6H_9(O)Cl$ to yield $[Cp^*Ru(\eta^6\text{-}C_6H_6)](CF_3SO_3)$ (**2**) in 60, 90, 35 and 90% yield, respectively; with 2,2,6,6-$C_6H_7Cl_4OH$ the reaction depends upon the conditions but in the absence of dihydrogen $[Cp^*Ru(\eta^6\text{-}C_6H_5OH)](CF_3SO_3)$ (**4**) is the major product, indicating a selectivity for C–Cl activation in the presence of C–O bonds; finally a new series of chlorinated clusters $[(Cp^*Ru)_3(\mu\text{-}Cl)_2(\mu\text{-}X)(\mu_3\text{-}CY)](CF_3SO_3)_n$ (X = Cl, Y = H, n = 1; **5**; X = CO, Y = H, n = 2: **6**; X = CO, Y = Cl, n = 2: **8**) is prepared in high yield from reactions of **1** with CH_2Cl_2 or 1,2-$C_6H_{10}Cl(OH)$.

Since the first demonstrations of the activation of carbon–halogen bonds through oxidative addition on Vaskas's compounds [1] such processes have been extensively studied. However activation of carbon-chlorine bonds by electrophilic metal centres does not appear to have received as much attention. Further, the problem of the presence of chlorinated hydrocarbons and in particular aromatic compounds in the environment has stimulated the search for dechlorination catalysts. Two recent reports describe the degradation of halogenated hydrocarbons through oxidation [2] or biphasic hydrogenolysis [3].

We have recently reported the preparation and reactivity of "Cp^*Ru^+" an electrophilic fragment with a great affinity for aromatic hydrocarbons [4]. Different aspects of "Cp^*Ru" chemistry have been developed by various research groups [5–12] and we have shown that this fragment is even able to activate C–H, C–C and C–O bonds [4f]. During study of reactions in CH_2Cl_2, we found out that the compound was able to activate the solvent, eventually producing a μ_3-carbyne moiety. We report in this communication the reactions of "Cp^*Ru^+" with various chlorinated hydrocarbons and deduce an order of reactivity of C–X (X = Cl, O, H, or C) bonds with it.

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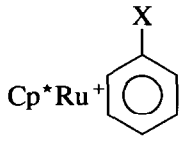


Scheme 1. Structure of π-arene derivatives of "Cp^*Ru^+", X = H:**2**; X = Cl:**3**; X = OH:**4**.

The "Cp^*Ru^+" fragment (**1**) is generated by protonation of [{Cp^*RuOMe}$_2$] with CF_3SO_3H as previously described [4e]. All reactions were carried out stoichiometrically (unless otherwise stated) in closed Fisher–Porter type vessels allowing gas analysis by GC. All solid products were characterized by NMR spectroscopy after evaporation of the reaction solutions to dryness, and comparison with authentic samples prepared from "Cp^*Ru^+" and the corresponding arene (**2–4**) or by recrystallization and use of classical methods such as microanalysis, infrared, ^1H and ^{13}C NMR spectroscopies, and X-ray diffraction for **5**, **6** and **8**. The conversions given are the percentage of transformation of the organic products.

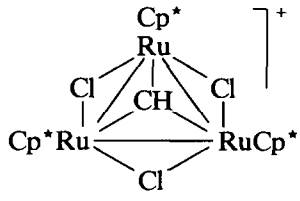
1 reacts at room temperature with $C_6H_{11}Cl$ to give [$Cp^*Ru(\eta^6$-$C_6H_6)$](CF_3SO_3) (**2**) in *ca.* 60% yield. Gaseous H_2 and HCl are also generated. The yield is probably limited by the competitive polymerization of THF. The same reaction occurs between **1** and *cis/trans* 1,2-$C_6H_{10}Cl_2$. It is very slow at room temperature but **2** is obtained nearly quantitatively at 80°C. The difference in reactivity between chloro- and dichloro-cyclohexane may be due to the prior coordination of the chloride groups to ruthenium [13]. In the first case C–H activation could occur rapidly, as observed for PCy_3 [14], whereas in the second case, the 5-membered ring may be stable enough to slow this reaction significantly.

Nevertheless, reaction of **1** with lindane (α-$C_6H_6Cl_6$) at 100°C yields a mixture of π-arene complexes in *ca.* 30% spectroscopic yield (as determined by ^1H NMR spectroscopy) with a 9:1 selectivity of **2** *versus* [$Cp^*Ru(\eta^6$-$C_6H_5Cl)$](CF_3SO_3) (**3**) *.

The preceeding reactions were also carried out under dihydrogen to determine whether catalytic hydrodechlorination could be performed on 50 equivalents of chlorocarbon using **1** as catalyst. Reactions under 1 atm H_2 in CH_2Cl_2 with $C_6H_{11}Cl$ (room temperature) and $C_6H_{10}Cl_2$ (80°C) led to the same results as before, formation of *ca.* 50% and over 90% of complex **2** respectively. No catalytic production of cyclohexane was detected.

In a further investigation, we attempted to establish competition between C–Cl and C–O bond activation. The latter bond had been previously found to be the easier to activate [4b]. The reaction of **1** with chlorocyclohexanone is rapid at room temperature in CH_2Cl_2 and yields **2** in over 90% yield. With chlorocyclohexanol in THF at room temperature only a *ca.* 10% conversion was observed, with a 10:1 selectivity for [$Cp^*Ru(\eta^6$-$C_6H_5OH)$](CF_3SO_3) (**4**) [4c] compared to **2**. At 80°C polymerization of THF occurs together with formation of a new trinuclear cluster

* An authentic sample of **3** was prepared by the usual method of preparation of π-arene complexes [4c]. ^1H NMR: δ 2.18 (s, C_5Me_5); 6.31 (m, C_6H_5Cl, *p*-H); 6.34 (m, C_6H_5Cl, *m*-H); 6.52 (m, C_6H_5Cl, *o*-H).



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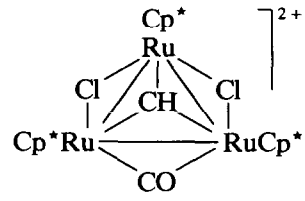

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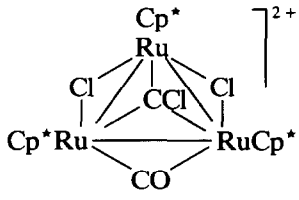

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Scheme 2. Proposed structure for clusters **5**, **6** and **8**.

(*vide infra*) in *ca.* 80% yield. These results are consistent with the previously observed higher reactivity of ketones compared to alcohols with "Cp^*Ru^+" [4f].

The most interesting reactivity was obtained with 2,2,6,6-tetrachlorocyclohexanol in different conditions:

- in THF at 60 or 80°C, the conversions were high (*ca.* 80%) with a selectivity of 1 : < 1 : 7 for **2**, **3**, and **4**, respectively.
- in CH_2Cl_2 at 80°C; the conversions were limited to *ca.* 30% with a 1 : 1 : 2 selectivity for **2**, **3**, and **4**.
- in CH_2Cl_2 under H_2, the conversions do not change (*ca.* 30%) but the selectivity is now 3 : 3 : 1 for **2**, **3** and **4**.

These results demonstrate the higher reactivity of C–Cl bonds in the absence of H_2 but are difficult to rationalize at the present time.

Finally, the reaction of **1** with CH_2Cl_2 leads quantitatively to a mixture of 3 clusters: $[(Cp^*Ru)_3(\mu\text{-}Cl)_3(\mu_3\text{-}CH)](CF_3SO_3)$ (**5**), $[(Cp^*Ru)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(\mu_3\text{-}CH)](CF_3SO_3)_2$ (**6**), and an uncharacterized green paramagnetic cluster (**7**) in 60, 30, and 10% yields, respectively. **5** has been previously prepared by Suzuki *et al.* by a different route [6c]. **5** and **6** were characterized by IR, ^1H and ^{13}C NMR spectroscopies and **5** by an X-ray crystal structure analysis which will be reported in a subsequent article. A related cluster $[(Cp^*Ru)_3(\mu\text{-}Cl)(\mu\text{-}CO)(\mu_3\text{-}CCl)](CF_3SO_3)_2$ (**8**) * was obtained in 80% yield from the reaction of **1** with

* $[(Cp^*Ru)_3(\mu\text{-}Cl)_3(\mu_3\text{-}CH)](CF_3SO_3)$ (**5**). ^1H NMR ($(CD_3)_2CO$): δ 1.83 (s, 45 H, C_5Me_5), 19.8 (s, ^1H, μ^3-CH). Microanalysis: Exp.: C, 39.3; H, 4.74. Found: C, 39.54; H, 4.46. $[(Cp^*Ru)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(\mu_3\text{-}CH)](CF_3SO_3)_2$ (**6**). IR (KBr) ν(CO): 1847 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 2.085 (s, 15H, C_5Me_5), 2.093, (s, 30H, C_5Me_5), 16.4 (s, 1H, CH). ^{13}C NMR ($(CD_3)_2CO$): δ 10.62 (q, J(CH) = 129.9 Hz, C_5Me_5), 11.34 (J(CH) = 129.9 Hz, C_5Me_5), 102.26 (s, C_5Me_5), 109.56 (s, C_5Me_5), 206.17 (s, CO), 340.57 (d, J(CH) = 177.0 Hz, CH). Microanalysis: Exp.: C, 36.50; H, 4.14. Found: C, 36.45; H, 4.09. $[(Cp^*Ru)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(\mu_3\text{-}C\text{-}Cl)](CF_3SO_3)$ (**8**): IR (KBr): ν(CO) = 1844 cm^{-1} (KBr). ^1H NMR ($(CD_3)_2CO$, Me_2CO-d_6). C_5Me_5: 2.09 (30H); 2.08 (15H). ^{13}C NMR ($(CD_3)_2CO$). C_5Me_5: 110.08; C_5Me_5: 10.76; 10.00; CO: 206.32. Microanalysis: Exp.: C, 35.41; H, 3.93. Found: C, 35.42, H, 4.03.

1,2-$C_6H_{10}Cl(OH)$ in THF. This suggests that the μ_3-methylidyne group does not arise from CH_2Cl_2 but from methanol, like the carbonyl group of **6** and **8**. These reactions are entirely reproductible (products and yields) but the mechanism of formation has not yet been elucidated.

In conclusion, the facile activation of carbon-chlorine bonds by the electrophilic "Cp^*Ru^+" fragment extends the chemistry of this fragment and leads to the following order of reactivity: C–Cl > C–O > C–H > C–C. Although the mechanism of these reactions is not yet fully understood, the selectivity and high yields of most of the transformations will allow a study of the reactivity of the new clusters. Finally, it is remarkable that even lindane can be dechlorinated in this way. Use of other electrophilic metal derivatives for this transformation is presently under study.

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