

Double C–H activation in pentamethylcyclopentadienylruthenium complexes

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Two methyls in each η^5 -C₅Me₅ are activated in $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$ **1 [by (i) air, (ii) *N*-chlorosuccinimide and (iii) air]; after carbonylation a mixture of the 1,3- and 1,2-isomers $[(\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2\text{Cl})_2)\text{Ru}(\text{CO})_2\text{Cl}]$ **4a,b** is obtained; the X-ray structure of **4a** is determined.**

There is considerable interest in the activation of methyls in pentamethylcyclopentadienyl complexes. This has been particularly so for ruthenium,¹ where the technique has allowed us to prepare new ranges of molecules that have the potential to act as catalysts, as well as for rhodium and iridium,² and for other metals.³

One C–H bond in pentamethylcyclopentadienylruthenium chloride **1** (or bromide) is easily cleaved under the influence of oxygen (1 atm, 20 °C, CHCl₃ solution). The reaction sequence has been shown to proceed *via* a μ -oxo dinuclear complex which effectively dehydrates to give the tetramethylfulvene complex **2**.¹ Carbonylation then gives the final product, the chloromethyl dicarbonyl complex **3**, obtained in 82% overall yield from **1** (Scheme 1).

We now report that the reactions can be repeated so that the C–H bonds on two different methyls (either 1,2- or 1,3-) of one ring are activated. To do this the above reaction sequence is carried out as far as the tetramethylfulvene complex **2**. This does not need to be isolated or purified but is treated directly with 2 equiv. of *N*-chlorosuccinimide (NCS) in CH₂Cl₂ (Scheme 2). A second aeration is then carried out, followed by a carbonylation (1 atm, 20 °C) to give a mixture of the red isomeric bis(chloromethyl)dicarbonyl chlorides, $[(\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2\text{Cl})_2)\text{Ru}(\text{CO})_2\text{Cl}]$ shown by NMR to be composed of **4a,b** in a 1 : 1 ratio. The complexes were separated by chromatography on a silica column (3 × 40 cm) in diethyl ether–light petroleum (bp 40–60 °C). Two bands were eluted, the first was shown by NMR spectroscopy and crystallography to be $[(\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2\text{Cl})_{2-1,3})\text{Ru}(\text{CO})_2\text{Cl}]$ **4a** (40% isolated yield),[†] while the second was shown by NMR to contain $[(\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2\text{Cl})_{2-1,2})\text{Ru}(\text{CO})_2\text{Cl}]$ **4b** (32% isolated yield).[†]

The isomers were initially identified by the relative positions of the ring methyls in the NMR spectra. As the CH₂Cl substituents deshield it was assumed that the complex with a single methyl signal at higher frequency than the two equivalent methyls was the 1,3 isomer **4a**, since the unique methyl is affected by two neighbouring CH₂Cl groups, while the 1,2

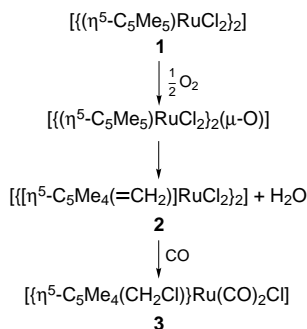
isomer **4b**, has the unique methyl at lower frequency since it lies between two methyls there. The assignments were confirmed by the crystal structure of the 1,3 isomer **4a**.

Similar reactions occurred when complex **1** was reacted with *N*-bromosuccinimide but in this case mixtures of isomers were formed that could be separated only with great difficulty.

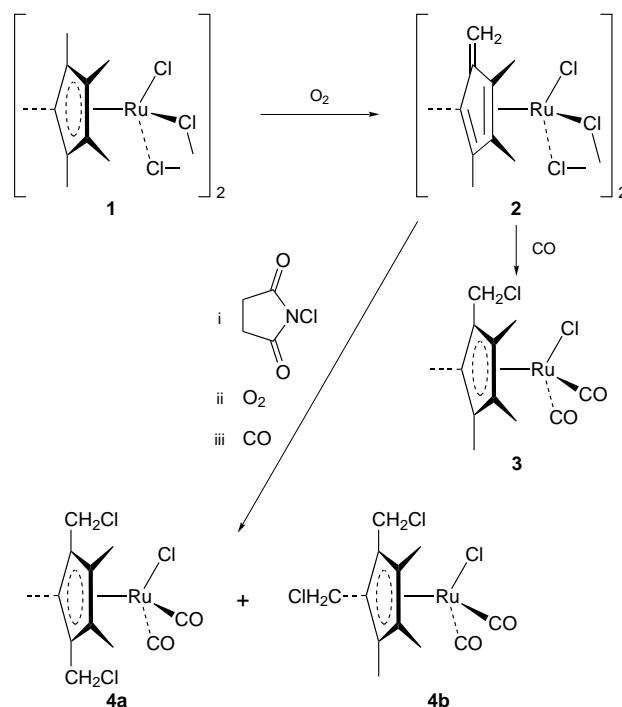
A crystal of complex **4a** for X-ray analysis was grown by slowly cooling a concentrated diethyl ether solution and leaving it at –23 °C for several days.[‡] The structure is illustrated in Fig. 1 and clearly shows the 1,3-arrangement of the chloromethyl substituents. The bond lengths are very similar to those previously found for complex **3**: Ru–Cl 2.409(2), 2.412(2) Å for **4a**; 2.422(3) Å for **3**; C–Cl 1.815(8), 1.812(7), 1.794(8), 1.806(8) Å for **4a**; 1.787(12) Å for **3**. As found in complex **3**, the Ru–C bond lengths to the carbons bearing the CH₂Cl substituents in **4a** are slightly shorter than the other Ru–ring C distances, but the differences are again only just significant.

Reaction of the isomeric mixture of **4a,b** dissolved in thf with a small amount of water and 2,4,6-trimethylpyridine gave a mixture of the two bis(hydroxymethyl) complexes **5a,b**,⁴ which were separated by chromatography on a silica column (eluent 7% MeOH in CH₂Cl₂), which gave two bands, the first contained $[(\text{C}_5\text{Me}_3(\text{CH}_2\text{OH})_{2-1,2})\text{Ru}(\text{CO})_2\text{Cl}]$ **5b**[†] (37% yield) while the second was found to be $[(\text{C}_5\text{Me}_3(\text{CH}_2\text{OH})_{2-1,3})\text{Ru}(\text{CO})_2\text{Cl}]$ **5a**[†] (28% yield).

Although several double activations of η^5 -C₅Me₅ ligands in early transition metal complexes are known,⁵ they are still rare for the late transition metals. However, we have previously noted sequential reactions⁶ and very recently two double activations have been reported. The rhodium and iridium



Scheme 1



Scheme 2

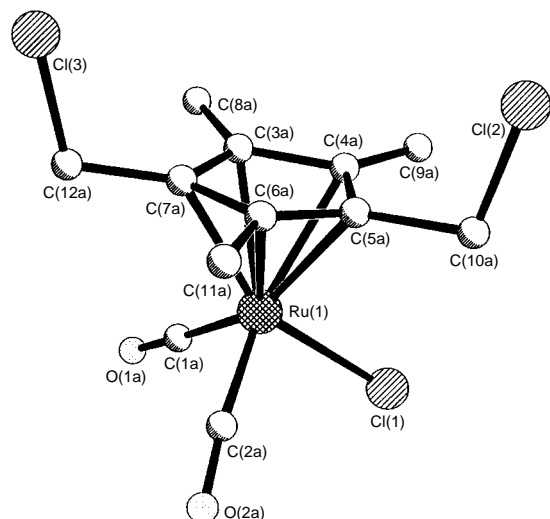


Fig. 1 Molecular structure of $[(\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2\text{Cl})_2\text{-1,3})\text{Ru}(\text{CO})_2\text{Cl}] \mathbf{4a}$ (hydrogens omitted)

complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) react with the diphosphine chelate $(\text{C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2$ to give $[\text{M}\{\eta^5\text{-C}_5\text{Me}_3[\text{CH}_2\text{C}_6\text{F}_5\text{P}(\text{C}_6\text{F}_5)\text{CH}_2]_2\text{-1,3}\}\text{Cl}]^+$ where a C–C bond has been formed by elimination of HF between two *ortho*-C–F groups of the ligand and 1,3-dimethyl groups of the $\eta^5\text{-C}_5\text{Me}_5$ ligand.⁷ In the other reaction $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ undergoes reaction with diphenylvinylphosphine in acetonitrile in the presence of potassium *tert*-butoxide to give a mixture of two complexes $[\text{M}\{\eta^5\text{-C}_5\text{Me}_3[\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{Ph})_2]\text{Cl}]^+$ where the C–H groups of two methyl groups (1,2- and 1,3-) have added to the vinyl groups.⁸ The mechanisms of neither of these reactions is clear, but ethanol solvent is required for the first, and base plays a significant role in the second. At present it looks as if the formation of **4** from **1** (or **2**) may involve radical intermediates of some type.

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Footnotes

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† *Selected spectroscopic data*: **4a**: $\nu(\text{CO})$ 2046, 1999 cm^{-1} (CH_2Cl_2); ^1H NMR (CDCl_3), δ 4.23 (m, $2 \times \text{CH}_2\text{Cl}$), 2.06 (s, Me), 2.04, (s, $2 \times \text{Me}$); ^{13}C NMR, δ 196.0 (CO); 110.2, 104.9, 92.3 [$\text{C}_5\text{Me}_3(\text{CH}_2\text{Cl})_2$]; 36.0 (CH_2Cl); 9.6, 9.5 ($2 \times \text{CH}_3$). **4b**: $\nu(\text{CO})$ 2046, 1999 cm^{-1} (CH_2Cl_2); ^1H NMR (CDCl_3), δ 4.28 (br, $2 \times \text{CH}_2\text{Cl}$); 2.11 (s, $2 \times \text{Me}$); 1.98 (s, Me); ^{13}C NMR, δ 196.3 (CO); 110.4, 106.1, 96.0 [$\text{C}_5\text{Me}_3(\text{CH}_2\text{Cl})_2$]; 35.2 (CH_2Cl); 9.9, 9.7 ($2 \times \text{CH}_3$). **5a**: $\nu(\text{CO})$ 2044, 1993 cm^{-1} (CH_2Cl_2); ^1H NMR (CDCl_3), δ 4.31 (br, $2 \times \text{CH}_2\text{OH}$); 2.55 (br, $2 \times \text{OH}$); 2.09 (s, $2 \times \text{Me}$); 2.03 (s, Me); ^{13}C NMR, δ 197.3 (CO); 104.7, 101.2, 98.2, [$\text{C}_5\text{Me}_3(\text{CH}_2\text{OH})_2$]; 55.0 (CH_2OH); 9.8, 9.7 (CH_3). **5b**: $\nu(\text{CO})$ 2044, 1993 cm^{-1} (CH_2Cl_2); ^1H NMR (CDCl_3), δ 4.28 (m, $2 \times \text{CH}_2\text{OH}$); 3.56 (br, $2 \times \text{OH}$); 2.01 (s, $2 \times \text{Me}$); 1.90 (s, Me); ^{13}C NMR, δ 197.1 (CO); 109.9, 103.8, 97.8, [$\text{C}_5\text{Me}_3(\text{CH}_2\text{OH})_2$]; 54.7 (CH_2OH); 9.8 (CH_3).

‡ *Crystal data for 4a*: $\text{C}_{24}\text{H}_{28}\text{Cl}_6\text{O}_5\text{Ru}_2$; $M = 811.30$; crystal dimensions $0.88 \times 0.42 \times 0.40$ mm. orthorhombic, space group $P2_12_12_1$ (D_2^4 , no. 19), $a = 8.9670(10)$, $b = 13.971(3)$, $c = 24.503(3)$ Å, $U = 3069.7(8)$ Å³, $Z = 4$, $D_c = 1.755$ g cm^{-3} , Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 1.538$ mm⁻¹, $F(000) = 1608$. Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 45^\circ$ on a

Siemens P4 diffractometer by the ω -scan method. Of the 2998 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 2743 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 . Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0398$ ($wR_2 = 0.1033$ for all 2811 unique data, 334 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum, maximum final electron density $-1.362, 0.573$ e Å⁻³. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0799 P)^2 + 1.2036 P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93⁹ as implemented on the Viglen 486dx computer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/420.

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