# Hydrogen Loss from Pentamethylcyclopentadienyl–Ruthenium Complexes; the Synthesis and X-Ray Structure of [Ru($C_5Me_4CH_2Cl$)$Cl_3$($Me_2S$)]

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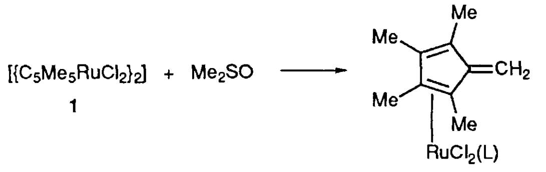
Reaction of [{$C_5Me_5RuCl_2$}$_2$] with $Me_2SO$ (in air in $CHCl_3$) gives [($C_5Me_4CH_2$)$RuCl_2$($Me_2SO$)], **2a**; this reacts with HCl to give [($C_5Me_4CH_2Cl$)$RuCl_3$($Me_2S$)] (also in high yield), characterised by an X-ray structure determination.

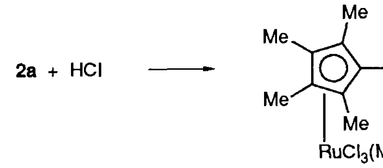
$\eta^5$-Pentamethylcyclopentadienyl complexes are generally characterised by considerable stability and low reactivity at the ring. Thus, for example, the $\eta^5$-$C_5Me_5$–Rh and –Ir complexes have only very recently been functionalised at a ring methyl.[1,2] The pentamethylcyclopentadienyl-Ru(III) chloride complex **1** has proved to be a versatile starting material for a range of reactions,[3] in most of which the $C_5Me_5$ ring retains its integrity.[4] We here report a very unusual, efficient and unexpected transformation in which a hydrogen is removed from one of the $C_5Me_5$ methyl groups.

Reaction of **1** with dimethyl sulphoxide ($CHCl_3$, 2 h, 20 °C) gave an orange $Me_2SO$ adduct, and in high yield (90%). However, the product was not the anticipated [$C_5Me_5$-$RuCl_2$($Me_2SO$)] but the tetramethylfulvene complex **2a**.† Attempts to grow crystals of X-ray quality have so far been unsuccessful, but the microanalytical and spectroscopic data are in complete agreement with the formula proposed; the complex is also monomeric in chloroform (by osmometry). The chemical shifts of the exocyclic methylene ($CH_2$) resonances suggest that it is coordinated, as in other tetramethylfulvene–ruthenium complexes, which have previously been characterised.[5]

Surprisingly, we find that the dehydrogenation of **1** does not seem to involve the dimethyl sulphoxide directly. No dimethyl sulphide is detected in the reaction, which does not, however, proceed under an entirely inert atmosphere; some air is required, probably forming water, and we suggest that the reaction proceeds according to eqn. (1).



**2a** (L = $Me_2SO$)
**2b** (L = $(CH_2)_4SO$)



**3**

$$2[\{C_5Me_5RuCl_2\}_2] + 4\ Me_2SO + O_2 \rightarrow$$
$$4[(C_5Me_4CH_2)RuCl_2(Me_2SO)] + 2\ H_2O \quad (1)$$
$$\mathbf{2a}$$

The presence of coordinated dimethyl sulphoxide in **2a** was confirmed by its reaction with tetramethylene sulphoxide (tetrahydrothiophene oxide) in $CDCl_3$. $Me_2SO$ was displaced, as indicated by the disappearance of the methyl signals at δ 3.08 and 3.22 and the appearance of a singlet (due to uncoordinated $Me_2SO$) at δ 2.6 in the NMR spectrum. The tetramethylene sulphoxide complex **2b**† was obtained from this solution and also, directly (85% yield), by reaction of complex **1** with tetramethylene sulphoxide.

Complex **2a** undergoes a further quite unexpected reaction with HCl gas in $CHCl_3$ to give complex **3** almost quantitatively (97%).† The structure was suggested by the spectra, and confirmed by a single crystal X-ray determination (Fig. 1).‡ This showed very clearly the presence of the Ru, three chlorines, an $\eta^5$-$C_5Me_4CH_2Cl$ ring, and that the remaining ligand on the metal was *not* dimethyl sulphoxide, as was

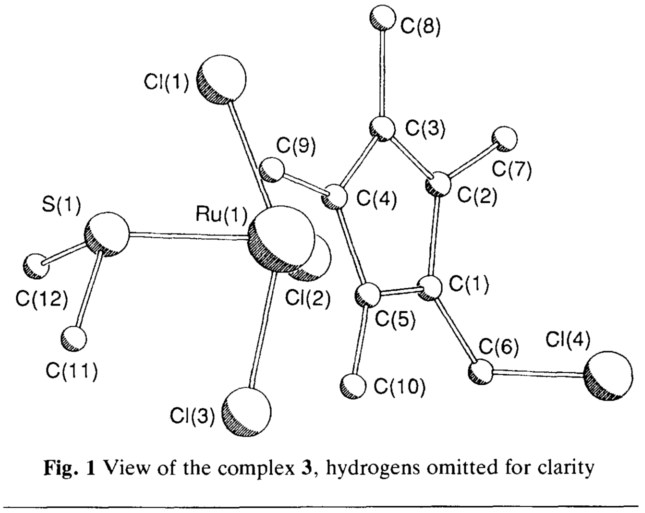


**Fig. 1** View of the complex **3**, hydrogens omitted for clarity

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† All new complexes gave satisfactory microanalytical results. Spectroscopic data (in $CDCl_3$) for **2a**: $^1$H NMR δ 1.69, 1.72, 1,86, 1.91 (4 × s $Me_4C_4$), 3.08, 3.22 (2 × s, $Me_2SO$), 4.90, 4.98 (2 × d, $CH_2$ $J$ 1 Hz); $^{13}$C NMR δ 8.2, 8.2, 9.2, 9.5 ($C_4\mathit{Me}_4$), 43.4, 45.0 ($Me_2SO$), 83.2 (=$CH_2$), 97.1, 99.7, 101.5, 104.1, ($\mathit{C}_4Me_4$), 114.6 ($\mathit{C}$=$CH_2$); ν(SO) 1106 $cm^{-1}$; for **2b**: $^1$H NMR, δ 1.72, 1.76, 1.88, 1.93 (4 × s; $Me_4C_5$), 2.17, 2.35, 2.93, 3.32, 3.72, 4.00 (mm, 8H, $C_4H_8SO$), 4.94, 5.02 (2 × d, =$CH_2$, $J_{HH}$ 1 Hz); $^{13}$C NMR δ 8.3, 8.7, 9.3, 9.7 ($\mathit{Me}_4C_5$), 25.8, 26.8, 57.3, 58.7 ($\mathit{C}_4H_8SO$), 83.1 (=$\mathit{C}H_2$), (97.6, 99.9, 101.8, 104.2 ($\mathit{C}_4Me_4$), 114.5 ($\mathit{C}$=$CH_2$); ν(SO) 1114 $cm^{-1}$; and for **3**: $^1$H NMR: δ 1.55, 1.69 (2 × s, Me on $C_5\mathit{Me}_4$), 2.39 (s, 6H, $Me_2S$), 3.97 (s, 2H, $CH_2Cl$). $^{13}$C NMR: δ 8.8, 9.5 (2 × s $C_5\mathit{Me}_4$), 22.5 (s, $Me_2S$), 35.8 (s, $CH_2Cl$), 100.4, 109.5, 111.1, ($\mathit{C}_5Me_4$).

‡ *Crystal data* for [$\eta^5$-$C_5Me_4CH_2ClRu(SMe_2)Cl_3$], **3**: $C_{12}H_{20}Cl_4RuS$, $M$ = 439.24, monoclinic, $a$ = 12.686(15), $b$ = 8.120(6), $c$ = 16.555(23) Å, $\beta$ = 97.05(10)°, $U$ = 1693(3) Å$^3$; $D_c$ = 1.719 g $cm^{-3}$, $Z$ = 4, space group $P2_1/c$ ($C_{2h}^5$, No. 14), Mo–Kα radiation ($\lambda$ = 0.71069 Å), $\mu$(Mo–Kα) = 16.49 $cm^{-1}$, $F(000)$ = 879.95. Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 four-circle diffractometer by the omega-scan method. The 2062 independent reflections for which $|F|/\sigma(|F|) > 6.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 7 azimuthal scans (minimum and maximum transmission coefficients, 0.359 and 0.458). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final $R$ 0.0782 ($R_w$ 0.0875, 163 parameters), with allowance for the thermal anisotropy of all non-hydrogen atoms; a weighting scheme $w^{-1} = [\sigma^2(F) + 0.00118(F)^2]$ was used in the later stages of refinement. Complex scattering factors were taken from the program package SHELXTL as implemented on the Data General DG30 computer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

expected, but dimethyl sulphide [Ru–S 2.418(4); S–Me 1.812(14), 1.807(15) Å]. The carbon, C(6), which was the *exocyclic* methylene in **2a** bears a chlorine in **3** [C(6)–Cl(4), 1.760(14) Å], bent well away from the metal. The $C_5$ ring is asymmetrically $\eta^5$-bonded, with C(1) slightly closer to the Ru [2.174(12) Å] than C(2)–C(5) [2.222(12)–2.337(12) Å]. The methyls C(7)–C(10), and C(6), are all bent away from the metal (above the least-squares ring plane).

Complex **3** is formally in the Ru(IV) oxidation state, a not uncommon one.[6] Negligible amounts of hydrogen (*ca.* 5%) are released in the reaction to form it, thus, the H from the added HCl must be acting to reduce the coordinated $Me_2SO$ to $Me_2S$, according to eqn. (2).

$$[(C_5Me_4CH_2)RuCl_2(Me_2SO)] + 2\,HCl \rightarrow \underset{\textbf{3}}{[(C_5Me_4CH_2Cl)RuCl_3(Me_2S)]} + H_2O \quad (2)$$

These experiments emphasise the versatility and variety of hydrogen transfer reactions promoted by Ru and show that ring methyl hydrogens can be involved.

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