Oxygen-Induced Methyl C-H Activation in (Pentamethylcyclopentadienyl)ruthenium Complexes

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Although pentamethylcyclopentadienyl (η^5-C_5Me_5, Cp*) is a spectator ligand in much of the chemistry of its transition metal complexes, we[2] and others[3,4] have found that C–H activation of ring methyls can occur (though often with some difficulty[2]), under the influence of strong bases or thermally. We now report that the oxygen–promoted cleavage of a C–H occurs with conspicuous facility in $C_5Me_5Ru^{III}$ complexes under ambient conditions. The products, Ru(II) complexes of tetramethylfulvene, exhibit unusual reactivity patterns leading to a wide and novel chemistry.

On exposure to air, a chloroform solution of $[\{(C_5Me_5)RuCl_2\}_2]$, **1**[5] (2 h, 20 °C), turned orange-red, to give, on workup, a diamagnetic orange-red solid, **3**, in essentially quantitative yield. The solid was stable for only a few hours at ambient temperatures, and it decomposed quite rapidly in solution. Elemental analysis and molecular weight measurements were consistent with the formulation $[\{(C_5Me_4CH_2)RuCl_2\}_2]$.[6] The ^{1}H and ^{13}C NMR spectra of **3** were complex and showed resonances arising from several different $C_5Me_4CH_2$ ligands, indicating the presence of isomers.

X-ray analysis of crystals of **3** showed[7] the presence of two crystallographically independent but virtually identical centrosymmetric $[\{(C_5Me_4CH_2)RuCl_2\}_2]$ dimers (Figure 1). The coordination about each Ru(II) was approximately octahedral, three sites being taken up by an η^6-tetramethylfulvene (Ru—C_5 ring carbons, average, 2.172(4) Å in molecule 1, 2.166(4) Å in molecule 2; Ru—CH_2, 2.268(4), 2.271(4) Å), the remaining three by one terminal (*trans* to =CH_2, Ru—Cl, 2.404(1), 2.410(1) Å) and two bridging chlorides (Ru—Cl, 2.468(1), 2.466(1) Å, and 2.468(1), 2.459(1) Å). The metal atoms are 3.662 Å apart and thus nonbonded. The C_5 ring is planar, with the attached methyls bent away from the metal, but the methylenic =CH_2 is bent toward the Ru by ca. 0.94 Å from the C_5 plane.

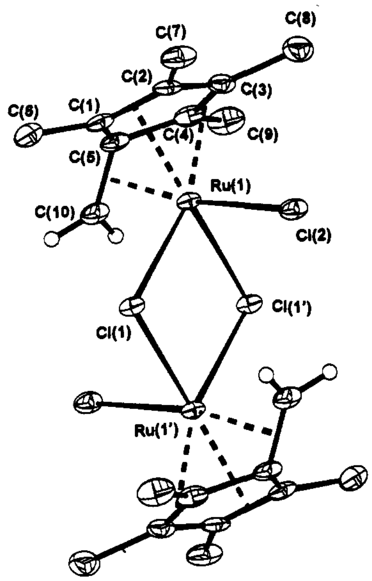

Figure 1. A view of the dimer (molecule 1) of $[\{(C_5Me_4CH_2)RuCl_2\}_2]$, **3**, from an X-ray crystal structure determination.

An intermediate in the oxidation of **1** to **3** is the μ-oxo complex **2**, which was recently synthesized and structurally characterized.[10] An oxygen titration, which showed 0.5 O_2 to be consumed for every molecule that reacted, therefore measured the transformation of the Ru(III) complex, $[\{(C_5Me_5)RuCl_2\}_2]$, **1**, into the Ru(IV) μ-oxide, **2** (eq 1 and Scheme 1); **1** contains both low-spin (diamagnetic) and high-spin (paramagnetic) dimers.[11]

$$\underset{\mathbf{1}}{[\{(C_5Me_5)RuCl_2\}_2]} + 0.5O_2 = \underset{\mathbf{2}}{[\{(C_5Me_5)RuCl_2\}_2O]} \qquad (1)$$

$$\underset{\mathbf{2}}{[\{(C_5Me_5)RuCl_2\}_2O]} = \underset{\mathbf{3}}{[\{(C_5Me_4CH_2)RuCl_2\}_2]} + H_2O \quad (2)$$

An anerobic chloroform solution of crystalline complex **2** (characterized by a singlet in the ^{1}H NMR spectrum at δ 1.78) was made under argon; after 30 min (25 °C), the characteristic ^{1}H NMR spectrum of **3** was obtained and water was detected (^{1}H NMR, δ 1.5). Thus no oxygen was required to transform the μ-oxide **2** into the new tetramethylfulvene complex **3** (eq 2).

Although ruthenium complexes are well-established as participants in organic oxidation and oxygenation processes,[12,13] this appears to be the first time that such a facile oxygenation leading

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(6) $[\{(C_5Me_5)RuCl_2\}_2]$, **1** (0.5 g), in chloroform (100 mL) was stirred in air (2 h/20 °C); concentration and addition of diethyl ether gave orange-red $[\{(C_5Me_4CH_2)RuCl_2\}_2]$, **3** (0.49 g, 100%). Acetone solutions of **3** were essentially nonconducting, 0.55 Ω^{-1} cm^2 mol^{-1}.

(7) Crystals of **3** were grown from chloroform–hexane (in the presence of dibenzothiophene as stabilizer); crystal data: $[\{C_{10}H_{14}RuCl_2\}_2 \cdot 3CHCl_3]$, M = 970.47; monoclinic, $P2_1/c$; a = 16.574(5) Å; b = 16.555(6) Å; c = 13.409(4) Å; β = 106.03(1)°; U = 3536(2) Å^3; Z = 4; D_{calcd} = 1.823 g cm^{-3}; $F(000)$ = 1912; T = 150 K. Intensity data were collected on a FAST area detector (details of the method are given in ref 8); 11 340 data were measured, giving 5609 unique reflections. The structure was solved by Patterson methods and refined on 5601 F_o^2 values using full matrix least squares (details of the method are given in ref 9). The final R factors were 0.041 and 0.031 respectively for all 5609 and 4168 observed [$I > 2\sigma(I)$] data and 394 parameters. Details of structure refinement and tables of atomic coordinates, bond lengths and angles, thermal parameters, and F_o/F_c have been deposited at the Cambridge Crystallographic Centre and are available as supplementary material. It may be noted than no dibenzthiophene was present in the crystal analyzed.

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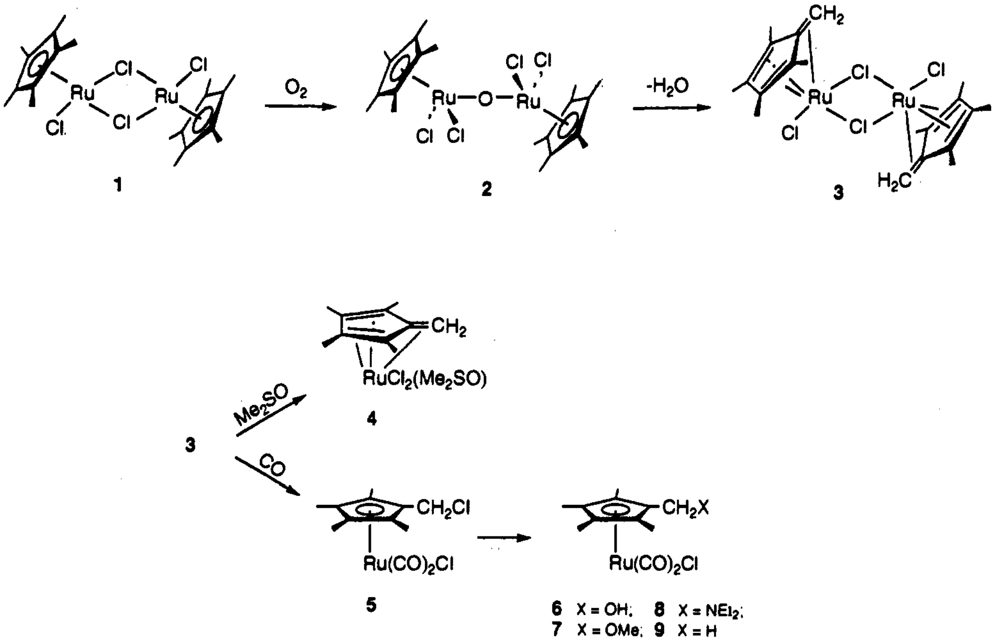
Scheme 1. Formation and Reactions of Complex 3



to a methyl C–H activation has been observed.[14] The more usual path from pentamethylcyclopentadienyl to coordinated tetramethylfulvene complexes, by the action of strong bases,[2,3] is not available for the conversion of **1** into **3** since the Ru:Cl ratio remains unchanged.

Cleavage of the Cl bridges occurred when the tetramethylfulvene complex **3** reacted with Me_2SO to give $[(C_5Me_4CH_2)RuCl_2(Me_2SO)]$, **4** (82%).[15] In sharp contrast, with CO (1 atm, 25 °C) it formed the dicarbonyl $[(C_5Me_4CH_2Cl)RuCl(CO)_2]$, **5** (85%), where one Cl has migrated onto the methylenic CH_2. This C–Cl was readily substituted by other nucleophilic reagents (e.g., H_2O/NEt_3, methanol, Et_2NH, or $NaBH_4$) to give $[(C_5Me_4CH_2X)Ru(CO)_2Cl]$ [**6**, X = OH (42%); **7**, X = OMe (89%); **8**, X = NEt_2 (78%); **9**, X = H (80%); respectively]. The activation of the CH_2–X bond to nucleophilic attack contrasts with the situation in rhodium,[2,14b] iridium,[2] and iron[14a] complexes which are attacked by electrophiles at the exocyclic CH_2. This allows functionalization of the Cp* ring with a whole new range of substituents and opens up a wide variety of novel chemistry, which will be reported on shortly.

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Supplementary Material Available: X-ray data on **3** and microanalytical, IR, and NMR data on complexes **3** and **5–9** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Methyl C–H activations which may be related have been reported: $[(C_5Me_5)Fe(C_6Me_6)] + O_2 \rightarrow [(C_5Me_5)Fe(C_6Me_5CH_2)]$[14a] and $[\{(C_5Me_5)Rh\}_2(O_2)(Cl)_2] + Me_3P \rightarrow [(\eta^4\text{-}C_5Me_4CH_2)Rh(R_3P)_3]Cl$.[14b] (a) Astruc, D.; Hamon, J.-R.; Roman, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502. (b) Hoard, D. W.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 612.

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