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Autoxidations of early transition metallocenes

II *. Bis(η^5-cyclopentadienyl)molybdenum(IV) dialkyls

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Abstract

Each of the compounds Cp_2MoR_2 ($Cp = \eta^5$-cyclopendadienyl, R = neopentyl or benzyl) in aromatic hydrocarbon solvent containing dissolved oxygen forms a weak complex at temperatures close to ambient ($\Delta H^\ominus$ for $Cp_2Mo(neopentyl)_2 \cdot O_2 = -9.1$ kJ mol^{-1}). At higher temperatures (60 °C) free radical autoxidation occurs ($t_{1/2} = 1.25$ h) to give a complex mixture of products.

Introduction

The importance of peroxidic early transition metal alkyl complexes was pointed out in Part I [1]. The peroxomolybdenum-catalysed epoxidation of propylene is an example of great commercial importance. Mimoun [2] has reviewed selective oxidations of organic compounds involving transition metal peroxy complexes. One route to transition metal alkylperoxides involves insertion of dioxygen into the metal–alkyl bond by means of free-radical, chain reactions. Brindley et al. [3] showed that homoleptic alkyls of tungsten and molybdenum reacted very rapidly with dioxygen; for example, the rate of the reaction of tetrabenzyltungsten(IV) was close to that corresponding to diffusion control at −74 °C, and hexaneopentyldimolybdenum(III) was slightly less reactive. It was later shown that upon introduction of two η^5-cyclopentadienyl groups onto zirconium(IV) alkyls to form a 16-electron metal centre, the autoxidations of the organozirconium compounds became manageable at room temperature [4]. The initiation step of the free radical chain reaction involved coordination of the molecular oxygen at the vacant orbital of the zirconium to give a weak superoxy complex.

$$Cp_2ZrR_2 + O_2 \rightarrow [Cp_2Zr(O_2)R_2] \rightarrow Cp_2Zr(O_2)R\cdot + R\cdot \qquad (1)$$

The final product was the dialkoxide, $Cp_2Zr(OR)_2$ obtained in high yield.

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* For Part I see ref. 1.

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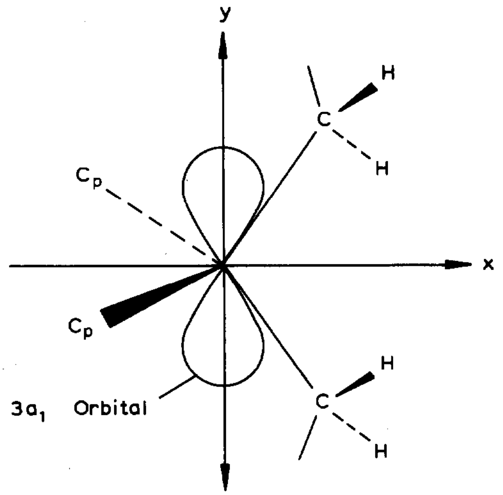

Fig. 1. Bonding orbitals in Cp_2MoR_2.

Green et al. [5] reported that bis(η^5-cyclopentadienyl)molybdenum dibenzyl is oxidized rapidly in air. $Cp_2Mo(CH_2Ph)_2$ is an 18-electron system with the lone pair of electrons in the $3a_1$ orbital which is aligned along the y-axis, with CH_2 groups in the yz-plane and the Cp groups in the xz-plane (Fig. 1) [6]. Initiation might not be expected to proceed as in eq. 1, and the present study was undertaken in order to establish the stoichiometry, kinetics, and mechanism of dialkylmolybdenocene autoxidations.

Results and discussion

Bis(η^5-cyclopentadienyl)molybdenum(IV) dibenzyl was prepared from the dichloride and the benzyl Grignard reagent. This gave a purer sample than that formed from the tetrameric lithio species $[LiMo(H)(\eta^5\text{-}Cp)]_4$ [5]. The dineopentyl analogue, $Cp_2Mo[CH_2C(CH_3)_3]_2$, was prepared from neopentyllithium. The autoxidations were studied at 60 °C by ^1H NMR spectroscopy and by measurement of the rate of oxygen absorption at constant volume by means of a pressure transducer [1,3]. That the reaction was a free radical chain reaction was confirmed by inhibition with phenothiazine, which is an effective peroxy radical trapping agent.

At temperatures close to ambient, solutions of either of the two molybdenocenes, in benzene or toluene saturated with molecular oxygen, showed a reversible line broadening of the ^1H NMR spectrum. This did not occur in deuterocyclohexane even though the solubility of oxygen is similar in all three solvents.

^1H NMR line broadening

As can be seen from Fig. 2 the effect of dissolved molecular oxygen on $Cp_2Mo[CH_2C(CH_3)_3]_2$ was to broaden the signals from the cyclopentadienyl and methylene protons. The same effect was observed with $Cp_2Mo(CH_2Ph)_2$. Aspiration of the solution with nitrogen gas caused the spectrum to return to that in degassed solvent. The presence at low levels of a paramagnetic compound such as oxygen is known to reduce the spin-lattice relaxation time and can cause the line widths to

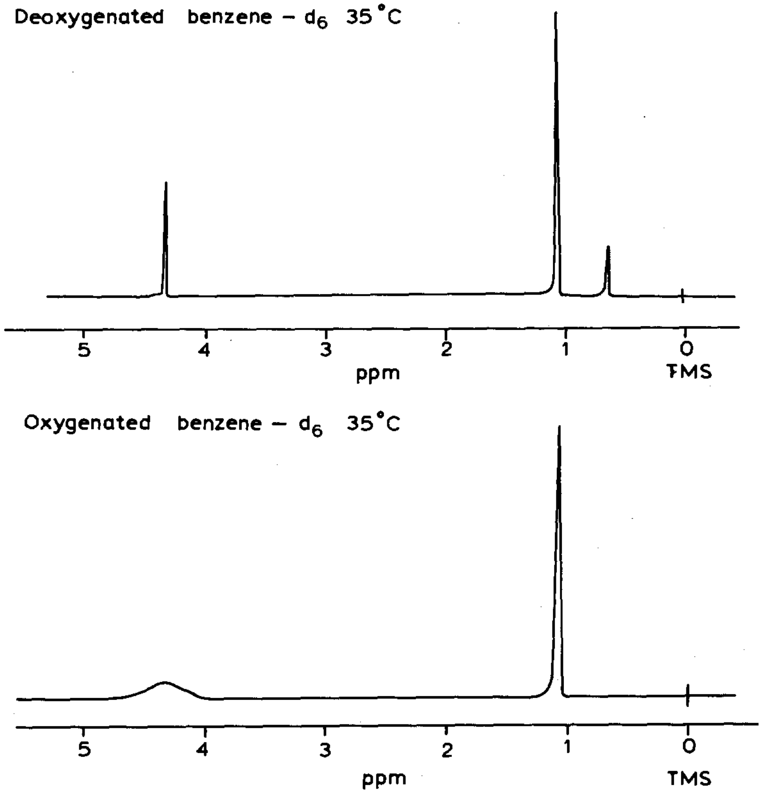

Fig. 2. ^1H NMR spectra of $(\eta\text{-}C_5H_5)_2Mo\{CH_2C(CH_3)_3\}_2$.

broaden in a ^1H NMR spectrum by about 0.2 Hz [7]. However, the line broadening in the case of the dialkylmolybdenocenes was 20 Hz or more and only certain peaks were broadened, the methyl and phenyl peaks being unaffected. Paramagnetic transition metal complexes can cause ^1H NMR line widths to broaden by as much as 1000 Hz, with line shifts of up to 300 ppm [8], but in the present case the peak positions were only a little changed. The interaction seems to involve a direct transfer of spin density to those protons closest to the molybdenum.

It is known that $Cp_2Mo(CH_3)_2$ can form an ionic complex with iodine to form the molybdenum(V) species [9], with donation of an electron to an iodine atom.

$$2\ Cp_2Mo(CH_3)_2 + I_2 \xrightarrow{Et_2O} 2[Cp_2Mo(CH_3)_2]^+ I^- \qquad (2)$$

The standard electrode potential and electron affinity of oxygen are much lower than for iodine and so a stable ion pair would not be expected with oxygen. The addition of chloroform to a degassed d_6-benzene-d_6 solution of $Cp_2Mo(CH_2Ph)_2$ showed a ^1H NMR line broadening effect similar to that of oxygen. It is known that chloroform will form weak charge-transfer complexes with certain donors. Examination by ESR spectroscopy of a tetrahydrofuran solution containing dissolved oxygen at $-40\,°C$ did not detect an ESR signal. The most reasonable explanation for the line broadening is that at near ambient temperatures in an aromatic hydrocarbon solvent containing dissolved oxygen there is a partial transfer of electron spin density from the molybdenum to the oxygen and that this is assisted by the charge-transfer properties of the solvent.

$$Cp_2Mo^{IV}R_2 + O_2 \xrightleftharpoons{\text{aromatic solvent}} (Cp_2MoR_2)^{\delta+} \cdot O_2^{\delta-} \qquad (3)$$

The rapid equilibrium lies largely to the left. Similar ^1H NMR behaviour has been observed for bis(salicaldehydato) bis(pyridine)cobalt(II) with low concentrations of pyridine [10] due to rapid exchange of pyridine between the free state and complexed sites.

When the ^{13}C NMR spectra of degassed and undegassed toluene-d_8 solutions of $Cp_2Mo[CH_2C(CH_3)_3]_2$ were compared, there was some broadening of the cyclopentadienyl carbon peak and the relative amplitude of all peaks except methyl decreased when oxygen was present. This is again attributable to a small amount of a paramagnetic component shortening the spin-lattice relaxation times. The infra-red spectra in benzene-d_8 did not vary with oxygen concentration; there was no band which could be attributed to the superoxide anion at 1145 cm^{-1}.

The visible electronic spectra in toluene showed a reversible shift of absorbance maxima to longer wavelength when oxygen was added. The effect was small for the neopentyl compound but pronounced for the benzyl compound.

Examination by variable temperature ^1H NMR

In the presence of dissolved oxygen the cyclopentadienyl protons peak shifted 0.3 ppm to higher field with a 150 °C lowering of temperature. The shift to higher field is in keeping with a positive spin density on the cyclopentadienyl protons as was previously found for nickelocenes and cobaltocenes [11]. It was found possible to estimate the standard enthalpy of formation, $\Delta H^{\ominus}$, if certain assumptions were made. From the straight-line plot of ln(field shift) against T^{-1} a value of -9.1 kJ mol^{-1} (Fig. 3) was obtained; this compares with the $\Delta H^{\ominus}$ for the charge-transfer complex between mesitylene and trinitrobenzene [12].

Autoxidation

The reversible interaction of Cp_2MoR_2 with molecular oxygen at temperatures close to ambient was accompanied by a slow absorption of oxygen over a period of some hours. However, at 60 °C the dibenzylmolybdenocene solution absorbed 2.5 molar equivalents of oxygen, producing first a dark green oil and then a black organic precipitate. These were accompanied by a large number of products which were sufficiently volatile to be detected by GLC. The dineopentyl analogue was similar in many respects (Table 1). In this case the black organic precipitate contained Mo, C, and H in a ratio of 1 : 11 : 14, and the mass spectrum had a peak $m/e = 281$ for ^{98}Mo. An IR band at 3110 cm^{-1} could be assigned to cyclopentadienyl C–H stretch. The autoxidations were inhibited by phenothiazine or galvinoxyl. Using the phenothiazine inhibition time for $Cp_2Mo(CH_2Ph)_2$ the rate of initiation was calculated to be 9.6×10^{-7} M s^{-1} for a 0.03 M solution.

It is possible that initiation involves the weak O_2 complex detected at lower temperatures. It is significant that $Cp_2Mo(neopentyl)_2$, in the absence of oxygen, undergoes thermal dissociation at 60 °C to liberate neopentane. Also the rate of formation of neopentane corresponds very closely to that of absorption of oxygen. It is therefore concluded that these bis(η^5-cyclopentadienyl)molybdenum dialkyls

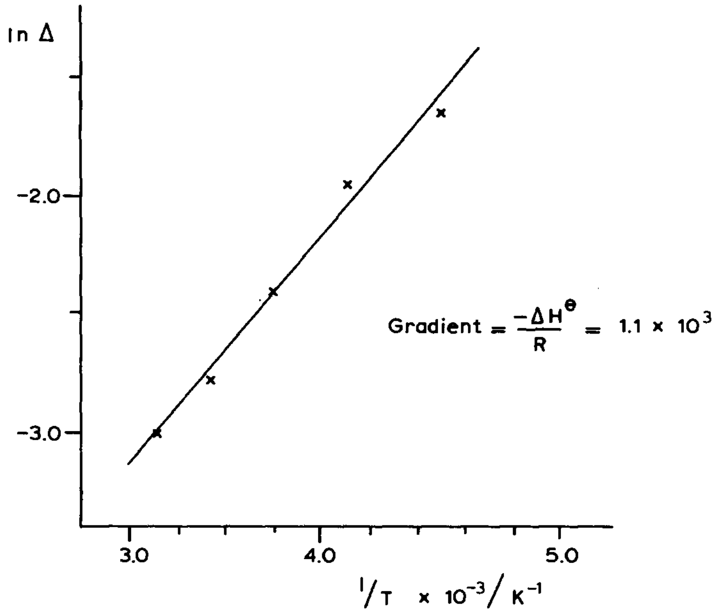

Fig. 3. Plot of ln (field shift) against T^{-1}.

readily undergo free radical autoxidation and the initiation is more likely to result from thermal homolysis of molybdenum–carbon σ-bonds.

$$Cp_2Mo^{IV}R_2 \xrightarrow{60\,^{\circ}} Cp_2Mo^{III}R + R\cdot \xrightarrow{2O_2} Cp_2MoR(O_2) + RO_2\cdot \qquad (4)$$

Experimental

Preparation of bis(η^5-cyclopentadienyl)molybdenum dialkyls

$Cp_2Mo(CH_2Ph)_2$. This compound was prepared from molybdenocene dichloride and the benzyl Grignard reagent [13]. To a slurry of Cp_2MoCl_2 (2.0 g, 6.7 mmol) in THF, (20 cm^3) at 0 °C, benzylmagnesium chloride in THF (0.42 *M*, 50

Table 1

Autoxidations of bis(η^5-cyclopentadienyl)molybdenocenes

	$Cp_2MoBenzyl_2$	$Cp_2MoNeopentyl_2$
Conc. (*M*)	0.03	0.02
Moles O_2 absorbed	2.5	2.0
Temp. (°C)	60	60
Order in metallocene	0	1
Order in oxygen	0	0.5
Initiation order in metallocene	–	–
R_i ($M\,s^{-1}$)	9.6×10^{-7}	–
$\frac{d[O_2]}{dt_0}$ ($M\,s^{-1}$)	5×10^{-6}	–
$t_{1/2}$ (h)	3	1.25

cm^3) was added dropwise with stirring. Stirring was continued for 4 h at 0 °C and then methanol (0.5 cm^3) was added and the brown mixture allowed to warm to room temperature. The volume was reduced to 20 cm^3 and transferred to a Florisil column (50 × 2 cm) in 40–60 petroleum ether; elution with petroleum ether and then with THF gave a brown band; this was eluted and the eluate cooled to −78 °C. Golden crystals separated and these were filtered off, washed with petroleum ether, and dried (0.84 g 31%). ^1H NMR (benzene-d_6) δ7.2–6.8 (m, Ph), 4.04 (sharp s, Cp), 1.97 (s, CH_2). Anal. Found: C, 70.59; H, 6.05. $C_{24}H_{24}Mo$ calc.: C, 70.51; H, 5.92%. MS: m/e 410 for $C_{24}H_{24}{}^{98}Mo$. Visible spectrum in degassed toluene λ_{max} 403 nm, ϵ_{max}420 and in aerated toluene, λ_{max} 411 nm, ϵ_{max} 380 mol^{-1} dm^3 cm^{-1}. In undegassed benzene-d_6 solvent the ^1H NMR spectrum showed a broad singlet at δ4.04 but the signals from benzylic CH_2 protons were no longer discernible. When the solution was flushed with nitrogen the spectrum reverted to that of the pure compound. The $Cp_2Mo(CH_2Ph)_2$ reported by Green et al. [5] as being formed from the tetrameric lithio complex had different properties from those above. When we used the tetrameric lithio procedure, the orange crystalline organometallic underwent autoxidation rapidly ($t_{1/2}$(25 °C) = 5 min) and ^1H NMR examination revealed the resence of two compounds. When molybdenocene diiodide was treated with the benzyl Grignard reagent in ether the same two compounds were formed, dibenzyl molybdenocene (60%) ($t_{1/2}$(60 °C) = 3 h) and a compound (40%) whose ^1H NMR data corresponded to those quoted by Green et al.

$Cp_2Mo(CH_2C(CH_3)_3)_2$. Neopentyllithium (4.72 g, 60 mmol) which had been isolated from n-pentane solution as a white solid, was redissolved and the solution was added to a slurry of Cp_2MoCl_2 (9.0 g, 30 mmol) in n-pentane at −78 °C. The mixture was allowed to warm to room temperature with stirring and then worked up as described for the dibenzyl analogue. The brown solution gave an orange band on elution with n-pentane and from the eluate orange-brown crystals were obtained (11%). ^1H NMR (benzene-d_6) 4.33 (s, Cp), 1.02 (s, CH_3), 0.59 (s, CH_2). Anal: Found: C, 66.3, H, 8.7. $C_{20}H_{32}Mo$ calc.: C, 65.2; H, 8.8%. MS: $m/e = 370$ $C_{20}H_{32}{}^{98}Mo$. In undegassed benzene-d_6 the 4.33 signal (Cp) became broad and the methylene protons were no longer detectable. The same effect was obtained when oxygen was bubbled through the degassed solution, and could be reversed by blowing nitrogen through the oxygenated solution. The ^{13}C NMR at spectrum at 35 °C (toluene-d_8 at 67.78 MHz did not show a variation in chemical shifts when the solution was oxygenated, but the line intensities changed except in the case of the methyl peak. Visible spectrum in degassed toluene: λ_{max} 398 nm, ϵ_{max} 220 mol^{-1} dm^3 cm^{-1}. The ^1H NMR shifts of the signals from the cyclopentadienyl protons were investigated over the range −90 °C to +60 °C in toluene-d_8 in the presence of dissolved oxygen. Abraham's method [12] was modified in order to provide an estimate of $\Delta H^\ominus$ in the temperature range +30 °C to −50 °C. The assumptions were made at $\Delta H^\ominus$ does not vary over the temperature range [14] and that in the absence of vortex stirring the oxygen concentration does not vary significantly. The difference, Δ, between the chemical shift for the cyclopentadienyl ring protons and that for pure $Cp_2Mo(CH_2C(CH_3)_3)_2$ is given by $\ln \Delta = -\Delta H^\circ/RT +$ constant. It can be seen from Fig. 3 that a linear plot was obtained (below −50 °C the linearity was lost);, from the gradient $\Delta H^\ominus = -9.1$ kJ mol^{-1}.

Infra-red absorption frequencies

$(\eta$-$C_5H_5)_2Mo(CH_2Ph)_2$ (KBr disc): 3120 (w), 3110 (w), 3090 (m), 3010 (m), 2960 (m), 2930 (m), 1510 (s), 1580 (m), 1485 (s), 1440 (m), 1430 (w), 1420 (m), 1365 (w), 1200 (m), 1180 (m), 1150 (m), 1125 (w), 1110 (m), 1075 (ms), 995 (ms), 905 (m), 865 (m), 840 (m), 830 (s), 815 (m), 760 (s), 750 (s), 710 (m), 690 (vs), 620 (w), 560 (m), 550 (s) cm^{-1}.

$(\eta$-$C_5H_5)_2Mo(CH_2C(CH_3)_3)_2$ (KBr disc): 3125 (w), 2980 (m), 2950 (s), 2900 (s), 2860 (s), 1475 (m), 1470 (m), 1455 (m), 1430 (m), 1380 (m), 1355 (s), 1230 (m), 1135 (w), 1120 (m), 1105 (w), 1065 (w), 1015 (m), 915 (w), 865 (s), 810 (w) cm^{-1}.

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