Journal of Organometallic Chemistry, 411 (1991) 131–137
Elsevier Sequoia S.A., Lausanne
JOM 21827

Autoxidations of early transition metallocenes

I. Bis(η^5-pentamethylcyclopentadienyl)zirconium(IV) dialkyls

J.M. Atkinson and P.B. Brindley *
Kingston Polytechnic, Penrhyn Road, Kingston upon Thames, Surrey KT1 2EE (UK)

(Received January 7th, 1991)

Abstract

Results of a study of the autoxidation of bis(η^5-pentamethylcyclopentadienyl)zirconium alkyls of the general formulae $Cp^{\star}_2ZrR \cdot X$ (where R = Me, CH_2Ph; X = R, Cl) and that of the mixed cyclopentadienyl $Cp^{\star}CpZr(CH_2Ph)_2$ are described. Rates of initiation and oxidation are compared with those for bis(η^5-cyclopentadienyl)zirconocenes.

Introduction

The oxidation of many air-sensitive organometallics has been shown to be a free radical chain process [1]. An understanding of the factors which govern the ease of autoxidation of early transition metal organometallics to form labile peroxides can lead to the design of air-stable organometallics or of compounds having a balance of thermal and oxidative properties likely to make them suitable as catalysts in organic oxidations, carbonylations, and polymerisations. We previously reported on the interaction of homoleptic zirconium, hafnium, molybdenum and tungsten alkyls [2] with molecular oxygen at temperatures as low as −74 °C, at which the rates of oxygen absorption were close to diffusion control. When two η^5-cyclopentadienyl groups were attached to zirconium or hafnium to form a 16-electron metal centre the bis(η^5-cyclopentadienyl) metal dialkyls had only one vacant site for coordination of oxygen at the initiation stage. The alkyl groups were selected to avoid β-hydrogen olefin elimination and were usually methyl, benzyl or neopentyl [3]. In these cases the rate of absorption of oxygen was measurable at temperatures not far from ambient. For example, bis(η^5-cyclopentadienyl)zirconium dibenzyl (0.1 *M* in toluene) had a half-life of 5 minutes at 45 °C and the final product was almost exclusively dibenzyloxy-bis(η^5-cyclopentadienyl)zirconium.

$$Cp_2Zr(CH_2Ph)_2 + O_2 \rightarrow Cp_2Zr(CH_2Ph)(OOCH_2Ph) \rightarrow Cp_2Zr(OCH_2Ph)_2 \qquad (1)$$

0022-328X/91/$03.50

The kinetic studies allowed recognition of the following stages in the mechanism:

Initiation

$$Cp_2ZrR_2 + O_2 \rightarrow [Cp_2Zr(O_2)R_2] \rightarrow Cp_2Zr(O_2)R\cdot + R\cdot \tag{2}$$

Propagation

$$R\cdot + O_2 \xrightarrow{\text{very fast}} ROO\cdot \tag{3}$$

$$ROO\cdot + Cp_2ZrR_2 \xrightarrow{\text{slow}} Cp_2Zr(R)OOR + R\cdot \tag{4}$$

Intramolecular rearrangement

$$Cp_2Zr(R)OOR \xrightarrow{\text{fast}} Cp_2Zr(OR)_2 \tag{5}$$

Marks [4] and Bercaw [5] have shown that the pentamethylcyclopentadienyl ligand possesses unique steric and electronic characteristics and provides improved solubility in hydrocarbon solvents. We now report on the effect on the autoxidations of zirconocenes containing two pentamethylcyclopentadienyl ligands, of the general formula $Cp^{\star}_2Zr(R)Z$ where $R = CH_3$, CH_2Ph or $CH_2C(CH_3)_3$ and $Z = R$ or Cl.

Results and discussion

The overall reaction of bis(η^5-pentamethylcyclopentadienyl)zirconium dialkyls with oxygen was significantly different from that of the unsubstituted dicyclopentadienylzirconium compounds. The absorption of oxygen was much slower; thus bis(η^5-pentamethylcyclopentadienyl)zirconium dibenzyl, $Cp^{\star}_2Zr(CH_2Ph)_2$, (0.1 *M* in toluene) had a half-life of ca. 2 hours at 60 °C, and although a total of 3 molar equivalents of oxygen were absorbed during 4 hours no benzyloxyzirconium derivatives were found. Significant amounts of toluene (2 molar equivalents) were generated within the first 10 minutes. When the autoxidation was carried out in benzene-d_6 no monodeuterated toluene could be detected, so it can be concluded that the hydrocarbon solvent plays little part in the initial stages of the autoxidation. Since no benzyl alcohol and benzaldehyde were detected, and because they are the normal termination products from benzylperoxy radicals, it is deduced that benzylperoxy radicals are not involved in the usual S_H2 displacement (4). Bis(η^5-pentamethylcyclopentadienyl)zirconium dimethyl behaved in a similar manner absorbing a total of 3 molar equivalents of oxygen over 48 hours at 50 °C. Methane was detected in the residual gas. Bis(η^5-pentamethylcyclopentadienyl)zirconium dineopentyl did not absorb oxygen at 60 °C during 48 hours even in the presence of the initiator tert-butyl hyponitrite; this might be expected for a molecule that is sterically hindered, particularly towards initiation (2) where oxygen is prevented from approaching the central zirconium. Because the toluene or methane is formed early on in the autoxidation it seems that a high proportion of the benzyl or methyl radicals formed at the initiation stage abstract hydrogen atoms intramolecularly from adjacent methylcyclopentadienyl groups. Intermolecular hydrogen abstraction must be minimal, since if benzyl or methyl radicals escaped from the cage environment then very fast peroxy radical formation would take place (3).

Table 1

Autoxidations of cyclopentadienyl- and pentamethylcyclopentadienyl-zirconium alkyls

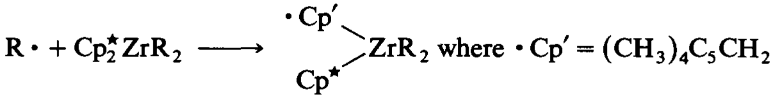
	$Cp^{\star}_2ZrMe_2$	$Cp^{\star}_2ZrBz_2$	$Cp^{\star}CpZrBz_2$	$Cp^{\star}_2ZrCl\cdot Bz$	Cp_2ZrBz_2 [3]
Conc. (M)	0.3	0.1	0.15	0.015	0.1
Moles O_2 absorbed per mole of initial complex	3	3	1.3	0.25	1
Temp. (°C)	50	60	45	30	55
Order in metallocene	1	1	–	–	1.55
Order in oxygen	–	0.5	–	–	0.5
Initiation order in metallocene	–	1	–	–	1
$R_i(M^{-1}s^{-1})$	–	2.5×10^{-6}	–	–	2.0×10^{-6}
$\frac{d[O_2]}{dt}(M\,s^{-1})$	–	5.8×10^{-5}	–	–	3.3×10^{-4}
$t_{1/2}$	14 h [a]	ca 2 h	3 h	7 min	5 min [b]

[a] In the absence of ^{t}Bu hyponitrite. [b] 45 °C. R_i = Rate of initiation.

The initial rates of oxygen absorption were directly proportional to the concentration of zirconocene. The primary initiation rates R_i in Table 1 were determined by use of phenothiazine as a free radical inhibitor and the relationship $R_i = n[\text{phenothiazine}]_o/\tau$, [3]. From the table it can be seen that these rates are very similar for the unsubstituted-cyclopentadienyl- and the pentamethylcyclopentadienyl-zirconocenes. It has been reported that the subsitution of two pentamethylcyclopentadienyl ligands for two cyclopentadienyl ligands has an electronic effect approaching that of a one-electron reduction of the metal [6] but in the case of reaction 2 this must be balanced out by the steric hindering effect of the methyl groups towards the approach of oxygen.

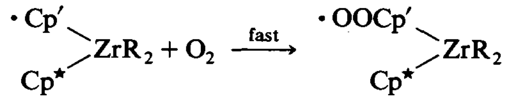
Superficially, the bis(η^5-pentamethylcyclopentadienyl)zirconium dialkyl oxidations closely resemble hydrocarbon autoxidations in that the oxygen absorption curves are sigmoid in shape, an effect that can be associated with hydroperoxide formation and autoinitiation (autocatalysis). In its simplest form the process would be:

Cage reaction

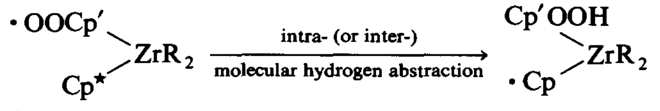


$$\mathrm{R}\cdot + \mathrm{Cp}^{\star}_2\mathrm{ZrR}_2 \longrightarrow \begin{matrix}\cdot\mathrm{Cp}'\\ \mathrm{Cp}^{\star}\end{matrix}{>}\mathrm{ZrR}_2 \text{ where } \cdot\mathrm{Cp}' = (\mathrm{CH}_3)_4\mathrm{C}_5\mathrm{CH}_2 \qquad (6)$$

Propagation



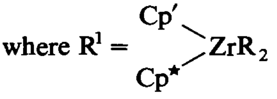
$$\begin{matrix}\cdot\mathrm{Cp}'\\ \mathrm{Cp}^{\star}\end{matrix}{>}\mathrm{ZrR}_2 + \mathrm{O}_2 \xrightarrow{\text{fast}} \begin{matrix}\cdot\mathrm{OOCp}'\\ \mathrm{Cp}^{\star}\end{matrix}{>}\mathrm{ZrR}_2 \qquad (7)$$



$$\begin{matrix}\cdot\mathrm{OOCp}'\\ \mathrm{Cp}^{\star}\end{matrix}{>}\mathrm{ZrR}_2 \xrightarrow[\text{molecular hydrogen abstraction}]{\text{intra- (or inter-)}} \begin{matrix}\mathrm{Cp'OOH}\\ \cdot\mathrm{Cp}\end{matrix}{>}\mathrm{ZrR}_2 \qquad (8)$$

Autoinitiation

$$\mathrm{R^1OOH} + \mathrm{Zr}^{n} \longrightarrow \mathrm{R^1O}\cdot + \mathrm{Zr}^{n+1} \text{ or } \mathrm{R^1OO}\cdot + \mathrm{Zr}^{n-1} \qquad (9)$$



$$\text{where } \mathrm{R}^1 = \begin{matrix}\mathrm{Cp}'\\ \mathrm{Cp}^{\star}\end{matrix}{>}\mathrm{ZrR}_2$$

The zirconium serves as a built-in redox initiator. At the end of the autoxidations described above numerous unidentified organic compounds were detected by GLC and ^1H NMR spectroscopy, but there was no evidence for any zirconium alkoxides. The other product was off-white zirconium oxide. The differences between the half-lives of the dibenzyl and dimethyl permethylzirconocenes can be attributed to the greater stability of the benzyl radical. It has previously been reported that bis(η^5-pentamethylcyclopentadienyl)titanium dimethyl gives methane by a thermal process [7], and it seemed possible that a thermal initiation rather than reaction 2 might also apply in the case of bis(η^5-pentamethylcyclopentadienyl)zirconium dibenzyl but this was ruled out because highly purified $Cp^{\star}_2Zr(CH_2Ph)_2$, uncontaminated with $Cp^{\star}_2Zr(CH_2Ph)Cl$, was stable at 90 °C in the absence of oxygen. However, thermal initiation cannot be ruled out in the case of $Cp^{\star}_2Zr(CH_3)_2$, particularly since the mass spectrum of the deutero compound $Cp^{\star}_2Zr(CD)_3)_2$ showed a molecular ion at $m/e = 377$, not 396 corresponding to a loss of CD_3H. The behaviour of the mixed cyclopentadienyl compound $Cp^{\star}CpZr(CH_2Ph)_2$ can be seen from Table 1 to be significantly different from that of the dicyclopentadienyl and the bis(pentamethylcyclopentadienyl)compounds. Thus it autoxidised very slowly ($t_{1/2}$(45 °C) = 216 min) and not at a rate intermediate between the other two. It does not give a sigmoid oxygen absorption curve and in this respect resembles $Cp_2Zr(CH_2Ph)_2$. There was no indication that a benzyloxy compound such as $Cp^{\star}CpZr(OCH_2Ph)_2$ was formed. It has been reported by Dixneuf [8] that a cyclopentadienyl along with a pentamethylcyclopentadienyl group attached to titanium dimethyl provide special stability.

Whereas bis-(η^5-pentamethylcyclopentadienyl)zirconium dichloride is air stable the benzyl derivative $Cp^{\star}_2Zr(CH_2Ph)Cl$ was found to be thermally unstable in hydrocarbon solvent in which it gave toluene at 30 °C, and also in the presence of oxygen, when it also gave toluene over a 15 min period and also formed a μ-oxo bridge dimer, $(Cp^{\star}_2ZrCl)_2O$. $Cp_2Zr(CH_2Ph)Cl$ had previously been shown to form the μ-oxo bridge dimer $(Cp_2ZrCl)_2O$ under similar conditions [3]. Phenothiazine, which was used to inhibit autoxidation and so allow determination of the rates of intiation given in Table 1, was not sufficiently effective towards $Cp^{\star}_2Zr(CH_2Ph)Cl$ to allow initiation-rate determination.

$$Cp^{\star}_2Zr(CH_2Ph)Cl \xrightarrow[\text{initiation}]{\text{thermal}}$$

$$Cp^{\star}_2Zr^{III}Cl + CH_2Ph\cdot \xrightarrow{O_2} \cdot Cp^1Cp^{\star}Zr(Cl)O_2 + PhCH_3 \quad (10)$$

Experimental

Bis(η^5-pentamethylcyclopentadienyl)zirconiumdichloride and cyclopentadienylpentamethylcyclopentadienylzirconium dichloride were prepared as described by Bercaw et al. [9,10]. Bis(η^5-pentamethylcyclopentadienyl)zirconium dimethyl and dideuteromethyl were prepared from the corresponding methyllithium species under argon in degassed solvents [5].

Dibenzyl- and (benzylchoro)-permethylzirconocenes

These were prepared from the dichloride and benzyllithium since the Grignard reagent was not sufficiently reactive below 80 °C.

$(C_5Me_5)_2ZrCl \cdot Bz$. To a slurry of $Cp^\star{}_2ZrCl_2$ (1.6 g, 3.6 mmol) in tetrahydrofuran (THF) (20 ml) at −70 °C was added benzyllithium (3.6 mmol) in toluene (5 cm^3) and THF (0.9 cm^3); the temperature was allowed to rise from −70 ° to 20 °C during 30 min. After a further 1 h a drop of methyl iodide was added, the red solution becoming orange. The solvent was replaced by toluene (10 cm^3) and petroleum ether (10 cm^3) and then cooled to −78 °C to give an orange precipitate (1.2 g, 68%). ^1H NMR (benzene-d_6) δ1.75 (s, CH_3), 1.69 (s, CH_2), 6.87–6.70 (m, Ph); Anal. Found: C, 66.2; H, 7.7; Cl, 7.8. $C_{27}H_{37}ClZr$ calc.: C, 66.4; H, 7.6; Cl, 7.3%.

$(C_5Me_5)ZrBz_2$. Even when an excess of benzyllithium was used the dibenzylzircononocene was contaminated with the monochloro compound, which was removed by repeated low temperature recrystallisation from equal volumes of toluene and petroleum ether; this resulted in a lower yield (22%). ^1H NMR (benzene-d_6) δ1.59 (s, CH_2), 1.68 (s, CH_3), 7.0 (m, Ph). Anal. Found: C, 74.7; H, 8.0; Cl, 0. $C_{34}H_{44}Zr$ calc.: C, 75.1; H, 8.1%.

$(C_5H_5)(C_5Me_5)Zr(CH_2Ph)_2$. To the mixed zirconocene dichloride, $CpCp^\star ZrCl_2$, (2.1 g, 5.8 mmol) in toluene (50 cm^3) at −78 °C was added an excess of benzyllithium in THF/toluene (0.65 *M*, 26 cm^3). After decantation and evaporation of the orange solution, the residual oil was dissolved in toluene (2 cm^3), *n*-pentane (10 cm^3) was added, and the solution cooled to −78 °C. The orange crystals were washed with 40–60 petroleum ether and dried to yield (cyclopentadienyl-pentamethylcyclopentadienyl)zirconium dibenzyl (0.5 g, 18%). ^1H NMR (benzene-d_6) δ7.0–7.4 (m, Ph), 5.58 (s, Cp), 1.74 (s, $Cp^\star$), 1.67 (s, CH_2). Anal. Found: C, 73.55; H, 7.29. $C_{29}H_{34}Zr$ calc.: C, 73.51; H, 7.23%.

$(C_5H_5)_2Zr[CH_2C(CH_3)_3]_2$. To bis(cyclopentadienyl)zirconium dichloride (2 g, 6.8 mmol) and neopentyllithium (1.9 g, 24 mmol) at −78 °C was added diethyl ether (50 cm^3) also at −78 °C. The stirred mixture was allowed to warm to room temperature (2 h). The excess of neopentyllithium was destroyed with methanol (0.5 cm^3), the solvent was removed under vacuum, and n-pentane (50 cm^3) was added. After filtration of the solution and cooling to −78 °C, lemon coloured crystals of $Cp^\star{}_2Zr(neopentyl)_2$ were obtained (1.3 g, 54%). ^1H NMR (benzene-d_6) δ5.88 (s, Cp) 1.05 (s, CH_3), 0.63 (s, CH_2). Anal. Found: C, 66.5; H, 8.4. $C_{20}H_{32}Zr$ calc.: C, 66.1; H, 8.9%.

$(C_5Me_5)_2Zr(OMe)_2$. Methanol was added at 20 °C to a stirred solution of bis(pentamethylcyclopentadienyl)zirconium dibenzyl (0.5 g, 0.9 mmol) in toluene (10 cm^3), and stirring was continued for 12 h. The solvent was removed under vacuum and the white solid recrystallised from toluene at −78 °C to yield the moisture sensitive dimethoxide. ^1H NMR (benzene-d_6) δ1.90 (s, CH_3), 3.97 (s, OCH_3).

Autoxidations of bis(η^5-pentamethylcyclopentadienyl)zirconium alkyls

These were carried out in freshly prepared toluene or benzene solutions. Oxygen absorption measurements were carried out at constant volume by use of pressure transducer as described in earlier publications [3,13].

$(C_{10}H_{15})_2Zr(CH_3)_2$. At 25 °C in toluene no absorption of oxygen occurred (25 h), but at 50 °C a molar equivalent of oxygen was absorbed (48 h). Since in the absence of initiator the self-initiation rate was too slow to measure, it was convenient to measure rates at 60 °C using di-tert-butyl hyponitrite initiatior (1×10^{-4} *M*).

The ^1H NMR signal from the zirconium-bonded methyl at δ −0.62 (in toluene − d_8) with initiator (6×10^{-3} *M*) disappeared completely after only 0.4 molar equivalents of oxygen had been absorbed (72 min). The IR spectrum of the residual gas from a similar autoxidation in benzene-d_6 showed methane to be present. After the autoxidation filtration gave an insoluble white solid, and work-up of the filtrate gave a brown sticky oil, the mass spectrum of which had highest *m/e* peak at 170.

$(C_{10}H_{15})_2Zr(CH_2Ph)_2$. At 30 °C the autoxidation was self-initiating and a total of 3 molar equivalents of oxygen were absorbed (16 h), but for convenience measurements were carried out at 60 °C (4 h). The initial rate of oxygen absorption was found to be directly proportional to the initial concentration of the dibenzylzirconocene. The initial rate of oxygen absorption was dependent on the partial pressure of oxygen air, being 2.3 times slower than in pure oxygen (0.082 *M* solution, 30 °C) $(-d[O_2]/dt)_0$, air = 1.55×10^6 *M* s^{-1}, pure oxygen = 3.57×10^6 *M* s^{-1}. Both galvinoxyl [11] and di-tert-butyl nitroxide [12] were found to be unsuitable as inhibitors since they interact with zirconocenes. Phenothiazine (3×10^{-3} *M* inhibited autoxidation and the inhibition time was inversely proportional to the initial zirconocene concentration.

^1H NMR spectroscopic examination of a benzene-d_6 solution after autoxidation (4 h) showed all the benzylic protons had been converted into toluene protons and the signals from the methyl substituents on the cylopentadienyl ligand had shifted from $\delta = 1.72$ (intensity 30) to 1.80 (intensity 12) ppm. The white solid from this autoxidation contained zirconium and showed IR bands (Nujol mull) at 1100(s), 1025(s) broad, 865(w), 800(s), 635(m) cm^{-1}.

$(C_{10}H_{15})_2Zr(Cl)CH_2Ph$. This chlorozirconocene (0.015 *M*) absorbed oxygen (0.25 molar equivalent) at 30 °C (15 min) and the maximum rate of oxygen absorption was at the start of oxidation. Toluene was detected by ^1H NMR spectroscopy among the products, and an off-white precipitate was isolated. The precipitate had a singlet in the ^1H NMR (spectrum benzene-d_6) at δ 1.82(s) ppm, and IR bands at 1263, 1100, 1025, 815(w), 800(s) cm^{-1}. The mass spectrum showed three groups of peaks with maxima at $m/e = 412$, 395, 276. The pattern of peaks with a maximum at $m/e = 412$ corresponded closely to that calculated for $(C_{10}H_{15})_2{}^{90}Zr(O)Cl^+$, and that at *m/e* 396 corresponded to $(C_{10}H_{15})_2{}^{90}Zr^{35}Cl$. When $Cp^\star{}_2Zr(Cl)CH_2Ph$ was dissolved in chloroform the dichloride $Cp^\star{}_2ZrCl_2$ was formed (60% yield) along with toluene.

Acknowledgements

The Borough of Kingston upon Thames is thanked for the award of a research assistantship to J.M.A.

References

1 P.N. Brindley, in S. Pataï (Ed.), The Chemistry of Peroxides, Wiley, New York, 1983, ch. 23.
2 P.B. Brindley and J.C. Hodgson, J. Organomet. Chem., 65 (1974) 57.
3 P.B. Brindley and M.J. Scotton, J. Chem. Soc., Perkin Trans. II, (1981) 419.
4 J.M. Manriquez, P.J. Fagan and T.J. Marks, J. Am. Chem. Soc., 100 (1978) 3939.
5 J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, J. Am. Chem. Soc., 100 (1978) 2716.
6 P.G. Grassman, D.W. Macomber and J.W. Hershberger, Organometallics, 2 (9183) 1470.
7 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Am. Chem. Soc., 94 (1972) 1219.

8 B. Demerserman, R. Make and P.H. Dixneuf, J. Chem. Soc., Chem. Commun., (1984) 1394.

9 J.E. Bercaw, J.M. Manriquez, D.R. McAlister, E. Rozenberg, A.N. Shiller, I.C. Sunney and K.L. Williamson, J. Am. Chem. Soc., 100 (1978) 3078.

10 J.E. Bercaw and P.T. Wolczanski, Organometallics, 1 (1982) 793.

11 F.D. Greene and W. Adam, J. Org. Chem., 28 (1963) 3550.

12 P.B. Brindley and M.J. Scotton, J. Organomet. Chem., 222 (1981) 89.

13 P.B. Brindley, J.C. Hodgson and M.J. Scotton, J. Chem. Soc., Perkins Trans. II, (1979) 45.