Journal of Organometallic Chemistry, 391 (1990) 189–194
Elsevier Sequoia S.A., Lausanne
JOM 20935

^1H and ^{13}C NMR evidence for the intermediate species $[(CpZrCl)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)]_2$. Cyclopentadienyl C–H bond activation by thermolysis of $[Cp_2Zr(H)Cl]_n$, $Cp_2Zr(R)Cl$, and $[Cp_2ZrCl]_2$

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(Received December 29th, 1989)

Abstract

Thermal decomposition at 80 °C of $[Cp_2Zr(H)Cl]_n$ (1) (Cp = η^5-C_5H_5), $Cp_2Zr(R)Cl$ (**2b**) (R = cyclohexyl) and $(Cp_2ZrCl)_2$ gives the fulvalenide dizirconium complex $[(CpZrCl)_2(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4\text{-}C_5H_4)]$ (**4**) via the intermediate $[(CpZrCl)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)]_2$ (**5**). Complex (**5**) can also be prepared by treating Cp_2ZrCl_2 with sodium amalgam (1.5 eq) in refluxing toluene. In the presence of cyclic polyenes, such as 1,5-cyclooctadiene (1,5-COD) thermolysis of **1** takes place at room temperature probably to give initially a labile π allyl species, which can be formulated in the case of the reaction with 1,5-COD as $Cp_2Zr(\eta^3\text{-}C_8H_{11})Cl$. This is the first example in zirconium(IV) chemistry of cyclopentadienyl C–H bond activation resulting in hydrogenation of unsaturated substrates.

Introduction

The complex $[Cp_2ZrH(CH_2PPh_2)]_n$ is known to be a good catalyst for active (and selective) hydrogenation of olefins (and diolefins) at 80 °C [1], a temperature at which it undergoes thermolysis to give two paramagnetic species, Cp_2ZrH and $Cp_2Zr(\mu\text{-}\eta^1:\eta^2\text{-}CH_2PPh_2)$ [2]. In contrast, Schwartz's reagent, $[Cp_2Zr(H)Cl]_n$ (**1**), although often used stoichiometrically in reaction with olefins to give the complexes $Cp_2Zr(R)Cl$ (**2**) by insertion of the olefin into the Zr–H bond [3], is not an effective hydrogenation catalyst [4].

By reduction of Cp_2ZrCl_2 with one equivalent of sodium amalgam, Cuenca and Royo [5] obtained $[Cp_2ZrCl]_2$ (**3**), and Herrmann and his colleagues [6] showed that

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† Dedicated to the memory of Professor D. Gervais.

reaction of 1.5 eq of Na/Hg with Cp_2ZrCl_2 gave $(CpZrCl)_2(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4\text{-}C_5H_4)$ (4), containing the $\eta^5:\eta^5$ fulvalenide ligand. The crystal structure of this complex was recently determined by Gambarotta et al. [7]. In other systems, abstraction of hydrogen from a cyclopentadienyl can give dizirconium complexes containing the η^1: $\eta^5\text{-}C_5H_4$ bridging moiety, and this is attributed to C–H bond activation by a zirconium(II) centre. Such reaction give $[Cp[\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4]Zr(PR_3)]_2$ complexes with evolution of H_2, as reported by Schwartz [8] and Alt [9] and their colleagues.

We report here the unexpected formation of the fulvalenide dizirconium derivative $(CpZrCl)_2$ $(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4\text{-}C_5H_4)$ (4) by thermolysis of $[Cp_2Zr(H)Cl]_n$ (1) or $Cp_2Zr(R)Cl$ (2), which takes place with evolution of H_2 or RH, respectively. Formation of an intermediate species (5) containing the $\eta^1:\eta^5\text{-}C_5H_4$ bridging moiety has been identified as the first step in the activation of a cyclopentadienyl C–H bond.

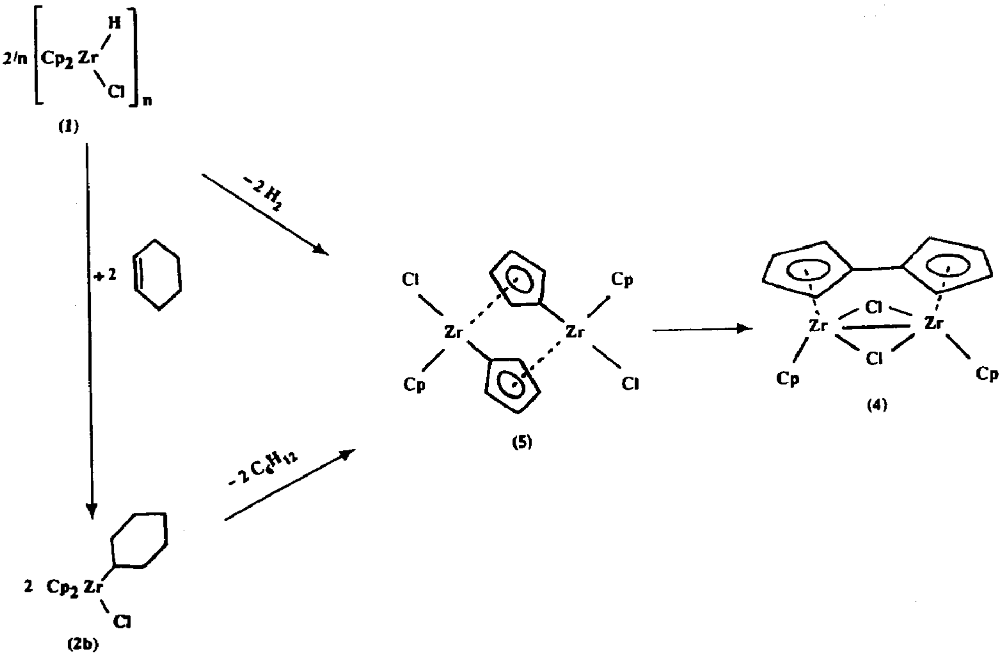
Results and discussion

To the best of our knowledge, no studies of the thermal decomposition of $[Cp_2Zr(H)Cl]_n$ (1) or $Cp_2Zr(R)Cl$ (2), have been reported, although Lappert and his colleagues [10] observed the formation of the short-lived (1 min) paramagnetic Cp_2ZrCl ($g = 1.980$) in photolysis of 1 and $Cp_2Zr(CH_3)Cl$ (**2a**). Thermal decomposition of a suspension of **1** and that of a solution of $Cp_2Zr(R)Cl$ (**2b**, R = cyclohexyl) [11] in C_6D_6 in a sealed tube takes place very slowly at room temperature, but more rapidly at 80 ° C, and the reaction has been monitored during some weeks by EPR, ^1H, and ^{13}C NMR spectroscopy.

With **1** and **2b** (as with **1** in the presence of unsaturated substrates such as cyclohexene and 1,5-cyclooctadiene) a dark red colour develops within 10 min at 80 ° C and weak EPR signals can be observed that give complicated spectra in which a doublet at $g = 1.983$ may probably be assigned to a Zr^{III} hydride ($a(^1H) = 5.8$ G) and while a broad singlet at $g = 1.960$ remains unassigned. A well-resolved singlet ($g = 1.979$, $a(^{91}Zr) = 42$ G) that can be assigned to Cp_2ZrCl [10] could be seen only in experiments carried out at room temperature, for example for **1** in the presence of cycloheptatriene. These unstable paramagnetic species disappear after ca. 1 h, the system gives no EPR signal, and a diamagnetic species can be identified by NMR spectroscopy, as the unexpected fulvalenide dizirconium derivative $(CpZrCl)_2(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4\text{-}C_5H_4)$ (**4**) formed via an intermediate species (**5**) containing the $\eta^1:\eta^5\text{-}C_5H_4$ bridging moiety, the generation of which is the first step in activation of a cyclopentadienyl C–H bond (Scheme 1).

The presence of **2b** and **4** in the reaction mixture (along with **5** was detected by comparison of their ^1H and ^{13}C NMR spectra with literature data [6,11]. The presence of Cp_2ZrCl_2 is always observed at the beginning of the reaction, and arises from a radical process [12].

The new complex **5** also was separately synthesized by a modification of the procedure previously described for **4**. Its ^1H NMR spectrum shows a Cp peak at 5.79 ppm and four multiplets of a AA'BB' system at 5.27 (2H), 5.18 (2H), 4.42 (2H) and 4.36 (2H) ppm. Irradiation of each of the multiplets clearly shows that the four ring protons are magnetically non equivalent. The $^{13}C\{^1H\}$ spectrum (Fig. 1) shows a Cp peak at 104.1 ($^1J(CP) = 171.8$ Hz) and resonances at 94.4 ($^1J(CH) = 179.8$ Hz), 98.1 ($^1J(CH) = 171.4$ Hz), 105.1 ($^1J(CH) = 174.0$ Hz) and 106.4 ($^1J(CH) = 170.6$ Hz)



Scheme 1

(attributable to C_5, C_2, C_3, C_4, respectively; C_1 unobserved) [13]. In view of the magnitude of the difference Δ (9.5 ppm) between the average chemical shift of C_5 and C_2 and that of C_3 and C_4, a structure containing a $\eta^1 : \eta^5$-C_5H_4 bridging moiety seems most likely (for fulvalenide species, Δ is < 5 ppm) [9]. Moreover **5** must be

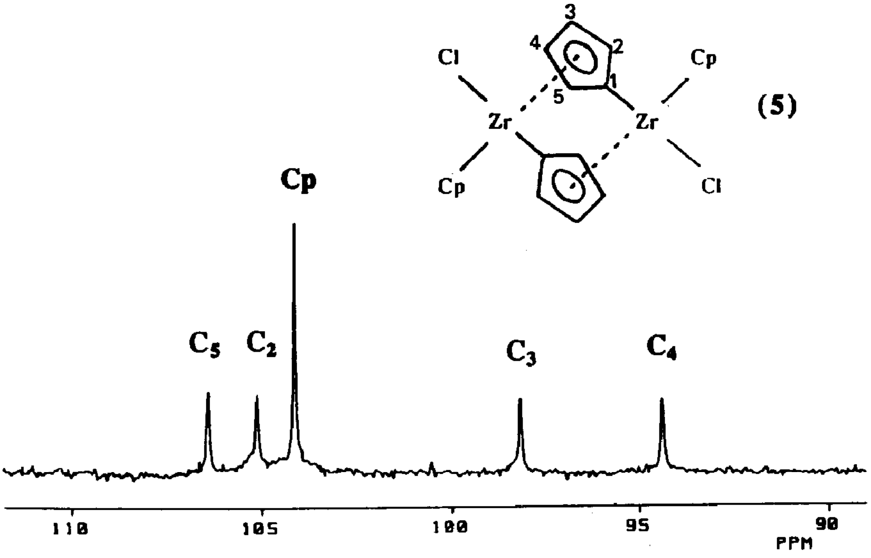


Fig. 1. ^{13}C NMR spectrum of $[(CpZrCl)_2(\mu\text{-}\eta^1 : \eta^5C_5H_4)]_2$ (**5**) (C_2, C_5 and C_3, C_4 can be interchanged).

an isomer of **4**, since the progressive transformation of **5** into **4** is accompanied by no other change in the composition of the reaction mixture, and in particular the amounts of cyclohexane (about 0.75 mol per equivalent of zirconium) and cyclohexene (a minor product).

Monitoring of the composition of the reaction mixture during the thermolysis shows that 20% of the zirconium is rapidly transformed into Cp_2ZrCl_2. The unchanged **2b** is progressively transformed into **5** which slowly isomerizes to the fulvalenide **4**, the appearance of which is detected after several hours at 80 ° C.

This sequence can be compared with that in the oxidation of $[(CpZr\text{-}\eta^1:\eta^5\text{-}C_5H_4)PR_3]_2$ by I_2, which gives the fulvalenide $(CpZrI)_2(\eta^5:\eta^5\text{-}C_5H_4\text{-}C_5H_4)$, the iodide analogue of **4**, via the very unstable $[CpZrI(\eta^1:\eta^5\text{-}C_5H_4)]_2$, the iodide analogue of **5**, which could be detected only at -50 ° C from its ^{1}H spectrum [8].

When the thermolysis of $[Cp_2Zr(H)Cl]_n$ (**1**) is carried out in the presence of a stoichiometric amount of cyclohexene, the course of the reaction closely parallels that for $Cp_2Zr(C_6H_{11})Cl$ (**2b**). For example, after 27 h at 80 °C, the mixture contains 0.10 **2b**, 0.20 Cp_2ZrCl_2, 0.50 **5** and 0.20 **4** together with 0.80% of cyclohexane.

In the presence of the cyclodiene 1,5-cyclooctadiene (1,5-COD) or the cyclotriene cycloheptatriene, $[Cp_2Zr(H)Cl]_n$ undergoes thermal decomposition at room temperature in a sealed tube in C_6D_6 or in THF. In C_6D_6 the formation of the intermediate **5** can be detected after one day and this is progressively transformed into the fulvalenide **4** during ca. 4 weeks, After this time, GLC showed that 81% cyclooctene, 17% 1,3-COD, and traces of 1,5-COD and cyclooctane were present.

The fact that the presence of a diene or triene leads to thermolysis at a temperature as low as 20 ° C, and that there is isomerization of 1,5- into 1,3-COD, may be attributed to the initial formation of a labile π-derivative, formulated as $Cp_2Zr(\eta^3\text{-}C_8H_{13})Cl$.

The important feature is that it is possible to activate a cyclopentadienyl C–H bond of $[Cp_2Zr(H)Cl]_n$ (**1**) or $[Cp_2Zr(R)Cl]$ (**2**) (either isolated or prepared in situ by reaction of the corresponding alkene with **1**), to give initially a species with a $\eta^1:\eta^5\text{-}C_5H_4$ moiety bridging two zirconium(IV) atoms. The reaction seems to driven forward by formation of H_2 or RH.

Especially noteworthy is that in the case of the system **1** + 1,5-COD there is C–H activation at room temperature with selective formation of cyclooctene.

A similar procedure starting from $(Cp_2ZrCl)_2$ also gives **4** and **5**, suggesting that the C–H cyclopentadienyl activation arises from the presence of the real or formal $Zr^{III}\text{–}Zr^{III}$ bond [8].

The rearrangement of a $(\eta^1:\eta^5\text{-}C_5H_4)$ to $(\eta^5:\eta^5\text{-}C_5H_4\text{-}C_5H_4)$ ligand seems general in zirconium and titanium chemistry [5–8].

In a complementary study, the behaviour of **1** as a hydrogenation catalyst was studied at 80 ° C and under 40 bar pressure of hydrogen. From an initial 150 eq of 1,5-COD, 30% cyclooctene and 70% cyclooctane were detected in the mixture after 15 h. A higher [1,5-COD]/[**1**] ratio leaves some unchanged 1,5-COD [14]. The ^{1}H NMR spectrum of the product mixture after oxidation reveals the presence of the fulvalenide oxo compound previously obtained by Hermann and colleagues [6a]. Complex **4** was found to be inactive for the catalytic hydrogenation of 1,5-COD.

The transformation of **1** (or **2b**) into **4** and **5** during catalytic hydrogenation provides an explanation of the poor catalytic activity of Schwartz's reagent.

Experimental

All experiments were carried out under argon by Schlenk tube and vacuum line techniques. All solvents (viz. benzene, toluene, tetrahydrofuran, pentane) were distilled from sodium benzophenone ketyl.

NMR spectra were recorded on a Bruker WH90 or WH250 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane (Me_4Si). ^1H NMR shifts are recorded relative to residual protiated solvent (benzene-d_5 δ: 7.15 ppm). ^{13}C NMR spectra were recorded at 62.90 MHz and chemical shifts are given relative to the solvent resonance (benzene-d_6 δ: 128.0 ppm). ESR spectra were recorded on a Bruker 200 TT spectrometer.

CPV analyses were performed on an Intersmat IGC 121 apparatus equipped with columns of Carbowax (10%, 2 m) or a Delsi 121 GC FDL equipped with capillary WCOT fused silica column (25 m).

The reagents 1,5-cyclooctadiene and cyclohexene (the latter distilled over Na) were passed through activated alumina column under argon immediately before use. Cp_2ZrCl_2, Cp_2ZrHCl, Cp_2ZrCl (cyclohexyl) and $(Cp_2ZrCl)_2$ were prepared as previously described [15,16,11,5].

Thermolysis were performed in sealed NMR tubes and monitored by NMR or/and ESR techniques. The progress of the reactions was monitored by use of the integrated signals from the cyclopentadienyl ligands in the ^1H NMR solution.

The catalytic reactions were carried out in a 100-ml stainless-steel autoclave under constant pressure (40 bar). The temperature was maintained at 80 °C by circulation of oil through a double jacket. The gas was contained in a tank connected to the autoclave. The fall in pressure in the thank was monitored with a pressure gauge connected to an electronic unit.

General procedure for thermolyzed experiments

In a typical experiment, a mixture of **1** (0.080 g, 31.0 mmol) and one equivalent of 1,5-COD (0.0335 g, 386 μl) was heated at 80 °C in a sealed tube. The brown-red solution initially gave an ESR signal (a doublet for a hydride species) but this disappeared rapidly and system was ESR-silent after approximately 1 h. Formation of **4** and **5** species was monitored by ^1H NMR spectroscopy by integration of the (η^5-Cp) peaks [δ Cp (ppm): 5.79 (**5**), 5.64 (**4**), 5.85 (**2b**)].

Synthesis of 5

A modification of the method used for synthesis of the fulvalenide zirconium complex **4** by gentle heating of a mixture of Cp_2ZrCl_2 and 1.5 eq of Na/Hg in toluene (60 °C, 1 h) gave $\{(Cp_2ZrCl)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)\}_2$ in 95% yield as a very air-sensitive microcrystals contaminated with a small amount of **4** (checked by ^1H NMR). Attempts to recrystallize **5** failed.

General procedure for catalytic experiments

In a typical run, a suspension of **1** (80 mg, 0.31 mmol) in 14 ml of THF and 5.8 ml of 1,5-COD (46.5 mmol) was introduced by syringe into the preheated (80 °C) autoclave and the gas was immediately admitted (40 bar H_2). Samples for GLC were removed by syringe from time to time.

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