Journal of Organometallic Chemistry, 399 (1990) C1–C3
Elsevier Sequoia S.A., Lausanne
JOM 21378PC

Preliminary communication

A binuclear alkenyl-bridged zirconium complex catalyzes the chemoselective hydrogenation of 1,3-cyclooctadiene to cyclooctene *

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(Received September 6th, 1990)

Abstract

The oligomeric hydrido zirconium complex $[Cp_2Zr(H)(CH_2PPh_2)]_n$ (1) reacts with (η^4-butadiene)zirconocene to yield the (μ-1-η^1:1,2-η^2-butenyl), (μ-phosphinomethylene) doubly bridged binuclear zirconocene complex $[Cp_2Zr(\mu\text{-}CH{=}CHC_2H_5)(\mu\text{-}CH_2PPh_2)ZrCp_2]$ 2. Complex 1 reacts with butadiene to give 2 and Ph_2PCH_3. At 80 °C complex 2 catalyzes the chemoselective hydrogenation of 1,3-cyclooctadiene to cyclooctene. Formation of a binuclear μ-alkenyl zirconium(IV)/zirconium(II) intermediate, similar to 2, is proposed to explain the effective protection of the remaining C=C double bond in the catalytic cycle.

In 1986 the Toulouse group reported a remarkably selective catalytic hydrogenation reaction of conjugated dienes to give exclusively mono-enes [1]. Thus, a catalytic amount of the oligomeric zirconium hydride $[Cp_2Zr(H)(CH_2PPh_2)]_n$, 1, at 80 °C induced the addition of dihydrogen to each of the cyclooctadiene isomers to give cyclooctene (> 98% selectivity). At the time the very nature of the active catalyst and thus the origin of this remarkable chemoselectivity remained unclear. Subsequently, it was found that the catalytic hydrogenation is of fractional order with respect to the oligomeric catalyst precursor 1, indicating some rate-limiting dissociative process of the active species [2]. We have now prepared a novel type of a binuclear μ-alkenyl, μ-CH_2PPh_2 doubly bridged binuclear zirconocene complex from 1 and butadiene, whose chemical features support the assumption that the catalyzed diene to mono-olefin hydrogenation may be one of the rare examples of bimetallic homogeneous catalysis, involving in this case the combined action of a

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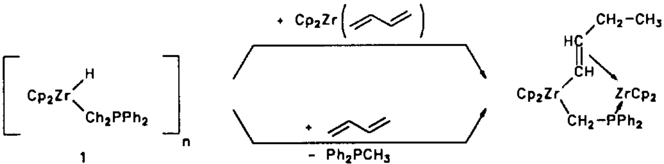
* Dedicated to the memory of Professor Daniele Gervais, untimely deceased on November 4th, 1989.

0022-328X/90/$03.50

zirconium(IV) and a zirconium(II) center to bring about rapid monohydrogenation and at the same time effective protection of the remaining C=C double bond.

The oligomeric [$Cp_2Zr(H)CH_2PPh_2]_n$, **1**, [3] was treated with one molar equivalent of (η^4-butadiene)zirconocene (ca. 1 : 1 *s-cis-/s-trans*-mixture) [4] at room temperature in THF. A single product was formed, which we identified as the [(μ-1-butenyl)(μ-phosphinomethylene)($ZrCp_2)_2$] **2** (see below). The same complex was formed independently when the oligomeric hydrido(phosphinomethylene)zirconocene **1** was allowed to react with butadiene. In that case, methyldiphenylphosphine was obtained as an additional stoichiometric reaction product.



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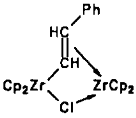

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Complex **2** turned out to be very reactive and extremely air and moisture sensitive, and this prevented its isolation. However, its very characteristic spectroscopic features allowed reliable structural characterization. The ^1H NMR spectrum of **2** (benzene-d_6, 300 MHz, ambient temperature) exhibits the signals of four inequivalent Cp-ligands, two of which show coupling with a phosphorus at zirconium [δ 5.64, 5.36, s, 5H each; 5.40 (J(PH) = 0.5 Hz), 5.13 (J(PH) = 1.1 Hz), d, 5H each]. Signals of a bridging phosphinomethylene group are observed at 0.9 (dd, 1H, ^2J(PH) = 4.0 Hz, ^2J(HH) = 11.5 Hz), 0.25 (d, 1H, ^2J(HH) = 11.5 Hz) and 7.0–7.8 (m, 10H, PPh_2). The ^1H NMR resonances of the μ-1-η^1 : 1,2-η^2-butenyl ligand appear at δ 5.0 (d, 1H, ^3J(HH) = 16.1 Hz, Zr-CH=), 2.97 (ddd, 1H, ^3J(HH) = 16.1, 8.2, 4.2 Hz, Zr-CH=C*H*–), 1.9 and 1.5 (m, 1H each, diastereotopic =CH–CH_2–), 1.3 (t, 3H, CH_3). The ^{13}P NMR resonance of the $-CH_2-PPh_2$ ligand is at δ −10.3. The ^{13}C NMR spectrum (75.4 MHz, benzene-d_6, ambient temperature) of **2** exhibits the $-CH_2PPh_2$ methylene resonance at δ 0.93 (dd, ^1J(CH) = 124 Hz, ^1J(PC) = 20.5 Hz). Four Cp signals appear at δ 108.5 (^1J(CH) = 170 Hz), 107.7 (^1J(CH) = 169 Hz), 103.7 (171 Hz) and 102.4 (171 Hz). The μ-1-η^1 : 1,2-η^2-$CH{=}CHCH_2CH_3$ moiety shows signals of the ethyl substituent at δ 39.5 (t, ^1J(CH) = 125 Hz, CH_2) and 21.1 (q, ^1J(CH) = 122 Hz, CH_3). Most characteristic for the specific bonding situation encountered here are the ^{13}C NMR features of the (μ-*C*H=*C*HR)[Zr]$_2$ moiety of **2**. Groups of signals are observed at δ 73.0 (dd, ^1J(CH) = 138 Hz, ^1J(PC) = 5.6 Hz, [Zr]–CH=*C*H–] and 149.9 (d, ^1J(CH = 106 Hz, [Zr]–*C*H=). Very similar ^{13}C NMR shifts and ^1J(CH) coupling constants have been found for the complex [($Cp_2Zr)_2$(μ-Cl)(μ-CH=CHPh)], **3**, the X-ray crystal structure of which has been reported in the literature (^{13}C NMR in benzene-d_6: δ 84.9 (d, ^1J(CH) = 145 Hz, [Zr]–CH=*C*HPh), 170.3 (d, ^1J(CH) = 108 Hz, [Zr]–*C*H=) [5]. The unusually low ^1J(CH) coupling constant for the α-CH=carbon seems to be very characteristic of the specific

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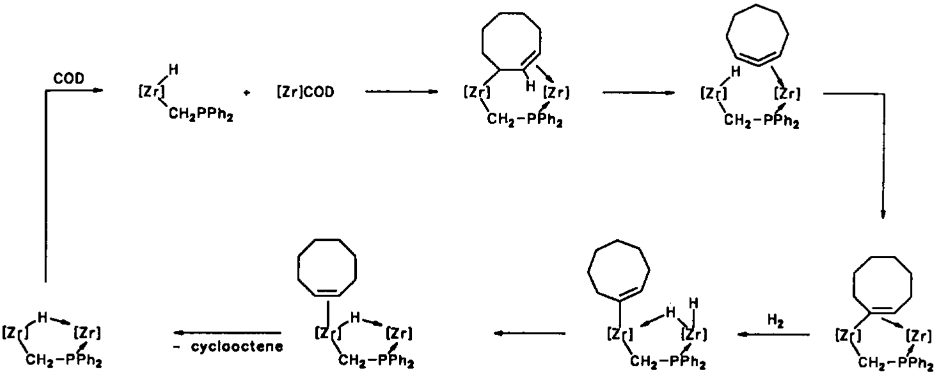
* Reference number with asterisk indicates a note in the list of references.



Scheme 1

bonding situation found in the μ-η^1 : η^2-alkenyl bridged binuclear zirconocene complexes [6].

Complex **2** catalyzes the hydrogenation of 1,3-cyclooctadiene under similar conditions to those used for the chemoselective diene hydrogenation induced by **1** (toluene solution at 80 ° C, 40 bar H_2, molar 1,3-cyclooctadiene/catalyst ratio: 300). The reaction rates and selectivities of the catalyst systems derived from complexes **2** or **1** are similar under these conditions. The cooperative effect of the zirconium(IV) and zirconium(II) centers, stabilized and held together by the bridging CH_2PPh_2-ligand in the suggested catalytic cycle (shown in Scheme 1), may account for the observed exclusive formation of the mono-olefin product cyclooctene.

Acknowledgement. Financial support from the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Alfried Krupp von Bohlen und Halbach-Stiftung (grants to G.E.) is gratefully acknowledged.

References and notes

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2 Recent investigations in the CNRS laboratory in Toulouse have revealed that use of the $[Cp_2Zr(H)CH_2PPh_2]_n$ hydrogenation catalyst **1** has advantages over other zirconium hydrides and in particular over $[Cp_2Zr(H)Cl]_n$, which tends to produce catalytically inactive paramagnetic zirconium(III) complexes under the conditions typically used [3]. Use of various concentrations of the catalyst precursor **1** and of the diene, and various H_2-pressures showed that the catalytic hydrogenation of 1,3-cyclooctadiene (1,3-COD) obeys the rate law $-d[1,3\text{-COD}]/dt \approx k[1,3\text{-COD}]^0\,[\mathbf{1}]^{1/2}\cdot p(H_2)$.

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