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First rhodium-catalyzed hydroformylation of cyclopentadiene

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ABSTRACT

This paper describes the first rhodium-catalyzed hydroformylation of cyclopentadiene (Cpd) using a homogeneous catalyst system consisting of $[Rh(OAc)_2]_2$ and the chelate ligand BISBI. At a reaction temperature of 100 °C and a syngas pressure of 30 bar the cyclopentane carbaldehyde is formed in 68% yield while 20% of the respective dialdehyde species are obtained within 3 hours. An important side reaction in Cpd hydroformylation reaction can be the dimerization of Cpd to its dimer dicyclopentadiene (Dcpd). This unwanted side reaction could be overcome by the use of tertiary alkyl amines as additives. Furthermore, the possibility to steer the reaction *via* the influence of the bite angle of diphosphine ligands was found.

1. Introduction

The transition metal catalyzed hydroformylation, discovered by serendipity by Otto Roelen in 1938 [1], is a very important reaction in industrial chemistry, which is carried out as a homogeneous reaction with cobalt or rhodium-based catalysts [2,3]. The advantages of the rhodium catalysts are the milder reaction conditions, the higher linear/branched ratio of the products and the higher activity [4]. The year 2008 saw the production of nearly 10.4 million tons of oxo chemicals [5], which impressively illustrates the great importance of the "oxo-products".

Cyclopentadiene (Cpd) is one of the most important components of the C5 fraction of the steamcracker with 25 weight% [6]. The separation of Cpd from the C5 fraction is carried out by dimerization of Cpd to dicyclopentadiene (Dcpd), which takes place at 30–100 °C at normal pressure. Further, Dcpd can be catalytically cracked to Cpd again, using copper or iron catalysts [7], by a retro-Diels-Alder reaction [8]. Cpd is stable only over a short period at −80 °C.

Till now only a few technical applications for Cpd are known [9]. For example it is used for the synthesis of polymers [10,11], ethylidenenorbornene [8], and ferrocenes [12,13]. The mono- and dialdehydes of Cpd can be used in different areas of the chemical industry, e.g. as building blocks for polymers, as well as fragrances [14,15].

Dcpd can be hydroformylated to mono- or dialdehydes respectively, which offer a broad range of applications. Through the industrially processed hydrogenation of Dcpd-dialdehydes dioles are obtained, which are used in polyesters or adhesives [16]. Furthermore, esters of Dcpd-diols are used in hydraulic fluids [17].

In literature the rhodium-catalyzed hydroformylation of Cpd is not described. So far, it was not possible to suppress the formation of Dcpd in hydroformylation completely. Only aldehydes of Dcpd can be obtained [14]. Therefore, the desired reaction, e.g. hydroformylation, has to be faster than the competitive dimerization process.

To the best of our knowledge the first successful hydroformylation of Cpd was investigated by Adkins at al. in 1952: hence, cyclopentane carbaldehyde was obtained as a main product in cobalt-catalyzed hydroformylation with 37% yield at 145–155 °C and 255 bar synthesis gas [18].

The great challenge was to find a catalytic system and specific reaction conditions to inhibit the dimerization and accelerate the hydroformylation process. In our work, we investigated the first rhodium-catalyzed hydroformylation of Cpd to the corresponding saturated C_6-aldehyde as main product.

2. Materials and methods

2.1. Laboratory experiments

All experiments were performed in an oxygen-free environment using standard Schlenk techniques. All reactions were performed in a 25 ml custom-made stainless steel autoclave [19]. In a typical

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Table 1
Hydroformylation of Cpd.

Run	Catalyst	Additives	Molar ratio Cpd:NEt_3	Solvent	Conv.[a](%)	Yield(%)			
						3	4	5	6
1.1	$[Rh(cod)Cl]_2$	–	–	Toluene	46	9	5	21	1
1.2	$Rh(acac)CO_2$	–	–	Toluene	38	11	6	12	2
1.3	$[Rh(OAc)_2]_2$	–	–	Toluene	55	26	5	18	4
1.4	$[Rh(OAc)_2]_2$	NEt_3	2:1	Toluene	90	56	18	8	2
1.5	$[Rh(OAc)_2]_2$	NEt_3	3:1	Toluene	76	32	6	14	5
1.6	$[Rh(OAc)_2]_2$	NEt_3	1:1	Toluene	77	38	13	15	2
1.7	$[Rh(OAc)_2]_2$	NEt_3	1:2	Toluene	44	26	4	7	1
1.8	$[Rh(OAc)_2]_2$	NEt_3	2:1	Cyclohexane	46	6	-	12	-
1.9	$[Rh(OAc)_2]_2$	NEt_3	2:1	THF	42	14	12	11	5
1.10	$[Rh(OAc)_2]_2$	NEt_3	2:1	DMF	12	3	-	6	-

Reaction conditions: 0.3 mol% precursor, 3 mol% BISBI, 5 mmol Cpd, 5 ml solvent, t = 3 h, T = 100 °C, 500 rpm, 30 bar CO.
[a] Conversion of Cpd determined by GLC.

experiment, the rhodium precursor and phosphorus ligand were first weighted out and then placed in an inerted Schlenk flask. Then the reactant (Cpd), the additive triethylamine and the solvent were added and placed in an ultrasonic bath until all solids were dissolved. The reaction mixture was transferred into the evacuated autoclave and pressurized to the desired syngas pressure. Then the autoclave was placed in a preheated oil bath at the chosen temperature. The magnetic stirrer was accelerated to 500 rpm. After the specified reaction time the reaction was stopped by rapidly cooling to room temperature using an ice bath. The excess syngas was expanded into the hood and the reaction mixture was taken out of the autoclave, weighted and then analysed by gas chromatography using di-*n*-butylether as internal standard and isopropanol as additional solvent if needed.

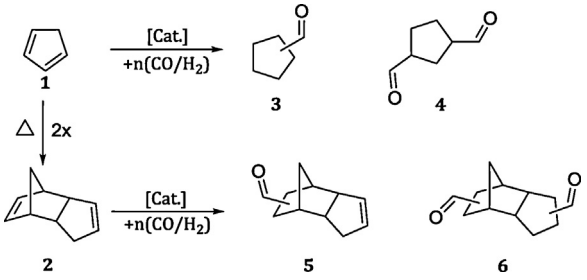
The experiments for the conversion time plot were conducted equivalent to the screening experiments, but with sampling of the reaction media at regular intervals. The reactor, a 300 ml steel autoclave (Parr instruments Company), was equipped with a sampling unit consisting of a capillary in combination with a dosing valve. This method allowed multiply sampling using the inner gas pressure inside the reactor for the reaction media sampling.

2.2. Chemicals

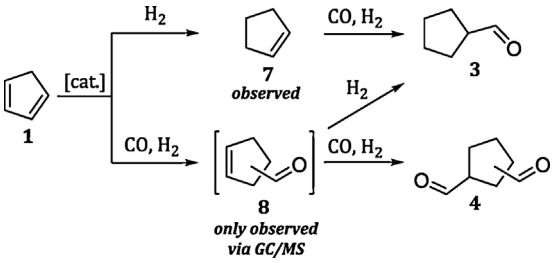
All non-aqueous solvents used in this work were purchased dryly from Acros Organics (Geel, Belgium) with a purity grade of >99%. Other chemicals were purchased from commercial suppliers and were of the highest purity available. They were used as received without further purification. Selected rhodium catalysts were purchased from Umicore AG & Co., KG (Hanau, Germany). The ligand BISBI ([2,2′-bis-((diphenylphosphino) methyl)-1,1′-biphenyl], >99.0%) was purchased from Acros Organics. Argon gas (99.998%, Messer Industriegase GmbH) and synthesis gas (99.9%, BASF) were used as received.

2.3. Analytics

Standard gas chromatographic analyses were performed on a HP 6890 instrument (Hewlett–Packard GmbH, Waldbronn, Germany) equipped with a flame ionization detector (FID) and a HP5 capillary column (30 m, diameter 0.25 mm, film thickness 0.25 μm) connected to an auto sampler. GC–MS analyses were carried out on a Hewlett–Packard 5973 (70 eV). All pure components have been calibrated to determine the conversion (X), yield (Y) and selectivity (S) of the reaction.



Scheme 1. Product range of the hydroformylation of Cpd and Dcpd.



Scheme 2. Possible reaction pathways in the hydroformylation of Cpd.

3. Results and discussion

3.1. Product range

Cpd was chosen as a cyclic 1,3-diene substrate for the studies on the hydroformylation reaction. Scheme 1 shows the product range of the hydroformylation of Cpd **1**. First, saturated mono- and dialdehydes of Cpd (**3** and **4**) can be directly obtained through the oxo synthesis. Dimerization of Cpd *via* Diels-Alder-reaction gives Dcpd **2**, existing both in *endo*- and *exo*-isomers, which leads to formation of respective monoaldehyde **5** and the dialdehyde **6**.

The formation of **3** is a result of a tandem reaction, which consists of selective hydrogenation of Cpd to cyclopentene **7** and subsequent hydroformylation to the respective saturated monoaldehyde (Scheme 2). Furthermore, cyclopentene was observed in low amounts as a byproduct after the reaction was performed.

Another way to obtain saturated monoaldehyde **3** would be first hydroformylation to the unsaturated cyclopentene carbaldehyde **8** and subsequent hydrogenation to the saturated monoaldehyde of Cpd. However, we did observe species **8** only in traces *via* GC/MS, so the formation of **3** from **8** has have to be very quick. On the other hand, cyclopentane dicarbaldehyde **4** was formed as a product in moderate yield, which is an obvious indication for existing of **8** as