First Spectroscopical Evidence of a Dioxomethylene Intermediate in the Reaction of CO₂ with Cp₂Zr(H)Cl: A ¹³C NMR Study

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Summary: An in situ variable-temperature ^{13}C NMR study on the mechanism of the reaction of Schwartz's reagent, $Cp_2Zr(H)Cl$, with labeled $^{13}CO_2$ was performed. In the course of the investigations, for the first time the long postulated $\mu\text{-}\eta^1\text{-}O,O'$ gem-diolate species $Cp_2Zr(Cl)$-$OCH_2OZr(Cl)Cp_2$ was observed.

Introduction

The hydrogenation of carbon dioxide to form methanol could be an important transformation of the greenhouse gas carbon dioxide into a useful C_1 chemical. Industrial processes for methanol production still use conversion of synthesis gas ($CO/CO_2/H_2$) over heterogeneous catalysts, a reaction introduced in the 1920s. Although known for a long time, the detailed mechanism of this reaction is still unclear. It is generally believed that initially the carbon monoxide in synthesis gas is converted into carbon dioxide.[1] One postulated pathway[2] proceeds further via a metal formate, which is then transformed into a dioxomethylene species (Scheme 1a). Addition of another hydrogen to the methylene carbon leads to a metal-bound methoxy species, which finally is hydrolyzed to methanol.

In this study we intended to test this postulated mechanism, by applying a model system that would facilitate NMR spectroscopic investigations. The reaction of the zirconocene hydrido complex $Cp_2Zr(H)Cl$ (Schwartz's reagent) with carbon dioxide, introduced by Floriani in 1978,[3] was particularly well-suited for these purposes. This system possesses, like many highly selective heterogeneous catalysts for conversion of carbon dioxide to methanol, a zirconium core as the hydride donor, and an identical mechanism was postulated for this reaction (Scheme 1b).[3] Although the course of the reaction was examined previously,[4] the intermediates could not be isolated or observed.

Results and Discussion

For all experiments we used samples containing a frozen suspension of $Cp_2Zr(H)Cl$ in deuterated THF, and 98 atom % ¹³C-labeled CO_2 was transferred in vacuo

Scheme 1. Reaction Pathways Proposed for the Catalytical Hydrogenation of CO₂ in Industrial Processes (a) and for the Stoichiometric Reduction of CO₂ with Cp₂Zr(H)Cl (b)
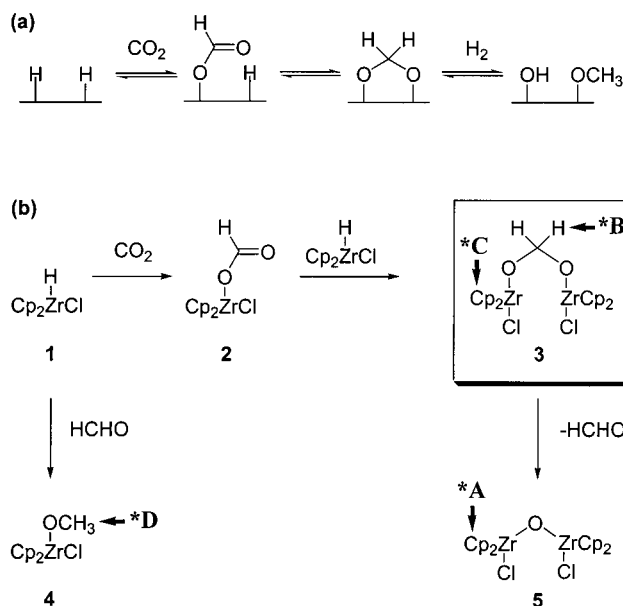
(details are given in the Experimental Section). ¹³C NMR measurements were first taken at 300 K (Figure 1).

Reactions were initiated by gentle shaking of the NMR tube, which allowed for suspension of the metal hydride **1** as well as dissolution of ¹³CO₂. Before the reaction was initiated only the signal of ¹³CO₂ at δ 125.8 could be observed. Shortly after initiation of the reaction a signal (***A**) at δ 114.9 appeared, which was subsequently assigned, by comparison to a standard sample, to the Cp residue of (Cp₂ZrCl)₂O (**5**), the reaction product.[5] The intensity of the signal increased, indicating the progress of the reaction.

By addition of more hydride to the solution another peak appeared at δ 101.2 (***B**). This initially very strong CH₂ carbon signal disappeared in less than 10 min, which is in accordance with the low stability of the postulated dioxomethylene species **3**. At the same time, a weak signal at δ 114.6 (***C**) was observable for 2 min, which was assigned, based on multiplicity, to be a Cp

(1) Wambach, J.; Baiker, A.; Wokaun, A. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5071−5080.
(2) Bart, J. C. J.; Sneeden, R. P. A. *Catal. Today* **1987**, *2*, 1−124.
(3) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269−270.
(4) Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877−2881.

(5) This signal was also observed in experiments run without added ¹³CO₂, indicating that (Cp₂ZrCl)₂O is likely present in the starting material as an impurity.
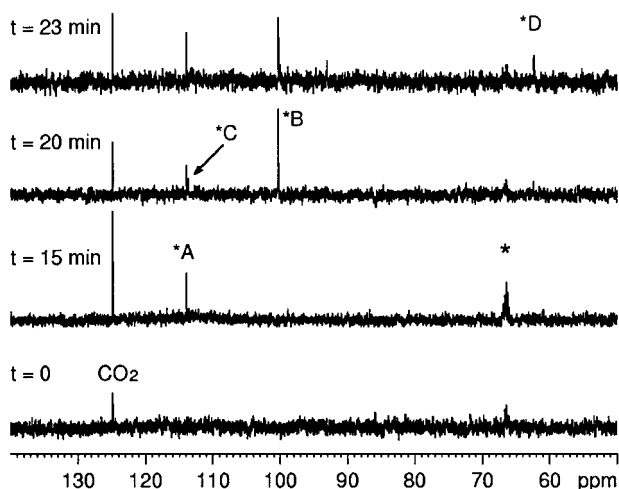
Figure 1. Observation of the reaction of $Cp_2Zr(H)Cl$ with $^{13}CO_2$. The spectra show the appearance of $(Cp_2ZrCl)_2O$ (*A), the dioxomethylene intermediate (*B and *C), and the methoxy compound $Cp_2Zr(OMe)Cl$ (*D). ^{13}C NMR spectra were recorded at 300 K (100 MHz, deuterated THF). The solvent signal is marked with an asterisk (*).
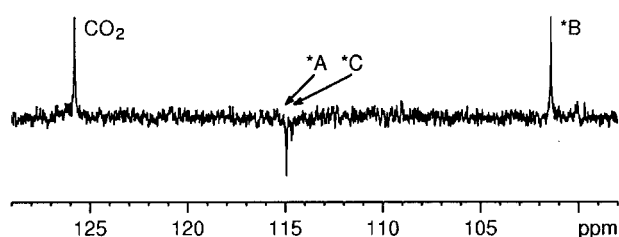

Figure 2. Expanded plot of a low-temperature ^{13}C APT spectrum, showing the number of protons attached to the carbons *B and *C of the dioxomethylene intermediate (235 K, 100 MHz, deuterated THF).

carbon. Finally, a CH_2 carbon signal with an intensity approximately equal to that of *C at δ 94.0 was observed, the origin of which is unknown. About 5 min after the first observation of *B and *C, a signal at δ 63.4 (*D) was detected, belonging to a CH_3 carbon. This signal was present during the entire measurement and is consistent with the metal-bound methoxy species Cp_2-$Zr(Cl)OCH_3$ (4),[6] presented in Scheme 1.

By performing low-temperature measurements in a temperature range 210–250 K, no changes in the order of appearance of the signals were observed, but the time period between the occurrence of *A and the detection of *B and *C was clearly longer. In addition, at 235 K the signal of *B could be observed for almost 60 min, but disappeared after heating the sample to room temperature. Appearing at the same time as *B, signal *C at δ 114.6, assigned to Cp carbons, slowly disappeared at temperatures greater than 235 K. On the basis of these observations, it is suggested that *B and *C both belong to the dioxomethylene species, 3. In the ^1H NMR spectrum at 210 K the protons of the ^{13}C-labeled dioxomethylene group appeared as a doublet at δ 5.36 (J_{CH} = 160 Hz). The chemical shift of the corresponding Cp protons could not be asigned.

At 210 K and at low concentrations of Schwartz's reagent a carbonyl carbon signal was observed at δ

177.2, almost simultaneously with signals *B and *C.[7] This signal's chemical shift was in agreement with that of the carbonyl carbon of the main isomer of $Cp_2Zr(Cl)$-OCHO (2), prepared as a reference sample in THF at the same temperature.[4] In ^1H NMR spectra a weak resonance was observed as a doublet at δ 8.25 (J_{CH} = 212). This was asignable to the formate proton of the major isomer of 2 after comparison to proton spectra of the reference sample as described above. At 210 K, these proton resonances could be observed until the tube was again agitated. Approximately 40 min after the first observation of the metal formate proton signals, a doublet at δ 3.84 (J_{CH} = 140 Hz) could be assigned to proton *D (4).[4] Also, after heating the sample to 273 K, an increasing concentration of formaldehyde was indicated by the growth in intensity of a doublet at δ 9.57 (J_{CH} = 178 Hz). During all measurements, definite assignments of the Cp resonances of $Cp_2Zr(Cl)OCHO$ (major isomer), $Cp_2Zr(Cl)OCH_3$, and $(Cp_2ZrCl)_2O$ in ^{13}C NMR were not possible, due to their very similar chemical shift (δ ca. 115) and broad line widths at low temperature.

In the course of our investigations of the in situ reaction of $Cp_2Zr(H)Cl$ with ^{13}C-labeled CO_2 we could for the first time observe the appearance of reaction intermediates, thereby providing support for the postulated mechanism in Scheme 1. The existence of the μ-η^1-O,O' gem-diolate species, 3, as well as metal formate 2, was shown by ^{13}C and ^1H NMR spectroscopy experiments. As a next aim, we hope to be able to confirm the proposed mechanism for our model system by studying a number of bridged zirconium complexes. These studies are a first step on the way to developing new homogeneous catalysts for CO_2 hydrogenation.

Experimental Section

All manipulations were carried out by standard high-vacuum and Schlenk techniques in the absence of air. Deuterated THF was distilled from a purple solution of sodium and benzophenone.

A pressure-stable NMR tube (Wilmad 522-PP) was charged with 10 mg (0.04 mmol) of $Cp_2Zr(H)Cl$ and 300 μL of deuterated THF. The mixture was degassed and frozen on a liquid nitrogen bath. On top of the frozen mixture ^{13}C-labeled CO_2 (0.05 mmol, 98 atom % ^{13}C) was transferred in vacuo, and the tube was sealed. For low-temperature measurements, the sample was brought to 195 K in a slurry bath and then transferred into the precooled magnet at 210 K. Due to the extremely low solubility of $Cp_2Zr(H)Cl$ in THF, no signal could be detected in the initial spectrum and only a weak signal of traces of dissolved $^{13}CO_2$ was observed. After carefully suspending some of the precipitated zirconium hydride,[8] achieved by gentle shaking of the NMR tube, the reaction with dissolved CO_2 took place. ^{13}C NMR spectra were recorded in a temperature range from 210 to 300 K with a repetition delay of 4.6 s and a 30° excitation pulse. The number of protons attached to carbons was checked by APT (attached proton test) spectra. All measurements were performed on a Bruker DRX 400 spectrometer with a 5 mm TBI probehead.

(6) Cénac, N.; Zablocka, M.; Igau, A.; Commenges, G.; Majoral, J.-P.; Skowronska, A. *Organometallics* **1996**, *15*, 1208–1217.

(7) The origin of a signal at δ 162.8, which was once observed at 235 K, remains unclear.
(8) This procedure was repeated before acquiring the room-temperature spectra at t = 15 min and t = 20 min. For the low-temperature measurements, additionally to the initial dispersion some more Schwartz's reagent was suspended 15 min after the first observation of *B (at 235 K) by agitating the NMR tube and, again, 30 min before the signal of *C was detected.