# Fast and reversible insertion of carbon dioxide into zirconcene-alkoxide bonds. A mechanistic study

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# Fast and reversible insertion of carbon dioxide into zirconocene-alkoxide bonds. A mechanistic study[†]

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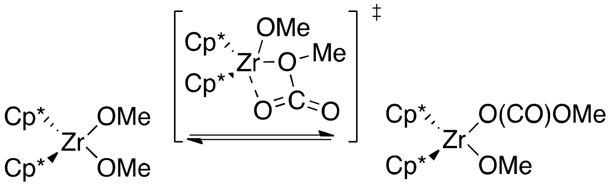
**(Graphical contents entry)**

In two consecutive equilibria the compound $(Cp^*)_2Zr(OMe)_2$ undergoes insertion of $CO_2$ to form the mono- and bis-hemicarbonates with a high rate.



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[†] Electronic Supplementary Information (ESI) available: NMR spectra and thermodynamic and kinetic data and figures. See DOI: 10.1039/c000000x/

**(Summary)**

In two consecutive equilibria the compound $(Cp^*)_2Zr(OMe)_2$ undergoes insertion of $CO_2$ to form the mono- and bis-hemicarbonates. Both equlibria are exothermic but entropically dis-favoured. Magnetisation transfer experiments gave kinetic data for the first equlibrium showing that the rate of insertion is overall second order with a rate constant of $3.20\pm0.12$ $M^{-1}s^{-1}$, which is substantially higher than those reported for other early transition metal alkoxides, which are currently the best homogeneous catalysts for dimethyl carbonate formation from methanol and $CO_2$. Activation parameters for the insertion reaction point to a highly ordered transition state and we interpret that as there being a substantial interaction between the $CO_2$ and the metal during the C–O bond formation. This is supported by DFT calculations showing the lateral attack by $CO_2$ to have the lowest energy transition state.

## Introduction

The use of carbon dioxide as a raw material is attractive in chemicals production since it is cheap, abundant and non-toxic. However, development has been hampered by the low reactivity of $CO_2$ and its activation using metal complexes has received considerable attention.[1] The direct synthesis of dimethylcarbonate (DMC) from methanol and $CO_2$ is among the most interesting possibilities not the least because it holds a promise to replace toxic C1-chemicals such as carbon monoxide, methyl sulfate and phosgene.[2] For this reaction there are still major challenges in terms of reaction rates and catalyst turnovers. Currently the best homogeneous catalysts are metal alkoxides based on tin, niobium or titanium.[3] Heterogeneous systems based on $ZrO_2$ have been reported,[4] but there are no reports on the use of zirconium based homogeneous catalysts for dialkylcarbonate synthesis from carbon dioxide. In all catalytic reactions the insertion of carbon dioxide into a metal-alkoxide bond is a key step and this has been reported for both early and late transition metals.[3,5] However, also in this respect there is an overall paucity of information on the reactivity of zirconium-alkoxide bonds towards carbon dioxide. One early study suggests that the $CO_2$ insertion in $Zr(OR)_4$ is thermodynamically favoured over the reaction with titanium,[6] and for zirconocenes it has been reported that $Cp_2Zr(OMe)_2$ is unreactive towards carbon dioxide.[7] Here, we report a detailed thermodynamic and kinetic investigation of the reversible insertion of $CO_2$ into the two alkoxide bonds of $Cp^*{}_2Zr(OMe)_2$ (**1**), showing that the reaction is fast and proceeds through a closed transition state. Theoretical calculations for the reaction are also reported.

## Experimental Section

**General procedures and materials.** All experiments were carried out under an atmosphere of nitrogen in a glovebox or using high vacuum-line techniques. All solvents were vacuum-transferred directly to the reaction vessel from sodium/benzophenone ketyl or calcium hydride. Zirconocenes $Cp^*{}_2ZrCl_2$ and $Cp^*{}_2ZrMe_2$ (**2**) were synthesised using literature procedures.[8] All commercially available reagents were purchased from Sigma Aldrich and used as received. Carbon dioxide was dried by passing the gas through a column of phosphorus pentoxide and then through a trap at -78 ˚C before being condensed into the reaction vessel. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer working at 499.77 MHz ($^1H$). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks as reference. NMR multiplicities are abbreviated as follows: s = singlet.

**Preparation of $Cp^*_2Zr(OMe)_2$ (1)** Approximately 50 mg of **2** (12.7 mmol) was added to a Strauss flask and after evacuation ca 30 ml of methanol was vacuum-transferred from sodium. Using an ultrasonic bath all **2** was dissolved. Stirring at room temperature for 12 h with removal of methane every ca 2 h gave complete conversion and pure **1** could be isolated after evaporating the methanol solvent. The NMR spectra were in agreement with the literature.[9] $^1H$ NMR ($C_6D_6$) δ 4.00 (s, 6H, $OCH_3$), 1.91 (s, 30H, Cp*). $^{13}C$ NMR ($C_6D_6$) δ 119.2 ($\mathit{C}_5Me_5$), 57.6 (Zr- O$\mathit{C}H_3$), 11.1 ($C_5\mathit{Me}_5$).

**Studies of $CO_2$ insertion in $Cp_2^*Zr(OMe)_2$.** A weighed amount of $Cp_2^*Zr(OMe)_2$ was transferred to a J. Young NMR tube and dissolved in $C_6D_6$. The solution was degassed by 2 cycles of freeze-pump-thaw on the high vacuum line. A measured amount of $CO_2$ was condensed into the tube to give the desired pressure prior to dissolution. The actual concentration will vary with pressure and temperature and was calculated from previously measured solubilities as determined by $^{13}C$ NMR spectroscopy by comparing the $CO_2$-peak with that of an internal standard.[10] After equilibration two compounds were characterised in solution in addition to **1**: **3** ($Cp^*_2Zr(OMe)(O(CO)OMe)$) and **4** ($Cp^*_2Zr(O(CO)OMe)_2$). **3**: $^1H$ NMR ($C_6D_6$) δ 4.08 (s, 3H, $OCH_3$), 3.53 (s, 3H, $OCO_2CH_3$), 1.86 (s, 30H, Cp*). $^{13}C$ NMR ($C_6D_6$) δ 158.9 (O$\mathit{C}O_2CH_3$), 120.5 ($\mathit{C}_5Me_5$), 58.2 (Zr- O$\mathit{C}H_3$), 53.4 ($OCO_2\mathit{C}H_3$), 10.9 ($C_5\mathit{Me}_5$).

**4**: $^1$H NMR ($C_6D_6$) δ 3.54 (s, 6H, ($OCH_3$)), 1.82 (s, 30H, Cp*). $^{13}$C NMR ($C_6D_6$) δ 159.2 (O*C*$O_2CH_3$), 121.8 (*C*$_5$Me$_5$), 53.6 ($OCO_2$*C*$H_3$), 10.8 ($C_5$*Me*$_5$).

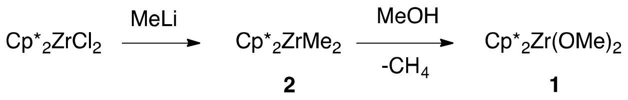
**Magnetization transfer experiments.** A J. Young NMR tube was filled with a 12.9 mM $Cp_2$*Zr(OMe)$_2$ $C_6D_6$ solution and pressurised with $CO_2$ as described above. The MeO $^1$H NMR peak of **1** at 4.00 ppm was selectively inverted using a shaped pulse constructed in the PBox routine of VNMR-J and peak heights of the MeO peaks of **1** and **3** were measured after different pulse-mixing times (from 30 ms to 4-5 times T1) using a non-selective 90˚ pulse. In the cases where peak widths changed during an experiment, peak areas were used instead. Spectra were collected as 8 repetitions with a 15-20 s relaxation delay. The exchange kinetics was evaluated using the CIFIT2[11] program. The perturbation of peaks from **4** was not significant and the second equilibrium was not included in the evaluation. All rate constants were treated as variables.

**Computational details**. All calculations were performed in Jaguar[12] using B3LYP-D3/LACVP*. The B3LYP-D3 functional combines the original B3LYP functional[13] with corrections for dispersion interactions.[14] The LACVP* basis uses the 6-31G* basis set for light elements, and the Hay-Wadt ECP with accompanying basis set.[15] Stationary points were validated by frequency calculations, and transition states were further validated by QRC[16] calculations. Energies in solvent were calculated with the PBF method using parameters for benzene.[17] Final free energies were calculated by adding the thermodynamic corrections from the frequency calculation to the calculated free energies in solvent.

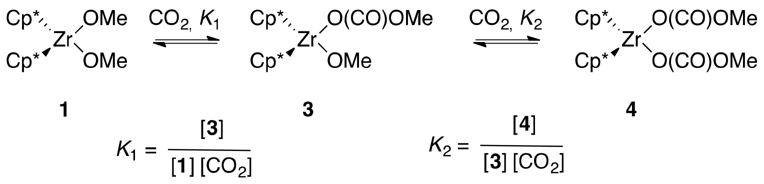
## Results and Discussion

$Cp^*_2ZrMe_2$ (**2**) was synthesised by literature methods, *cf.* Scheme 1.[8] To obtain $Cp^*_2Zr(OMe)_2$ (**1**) we modified a literature procedure starting from the bis(benzyl)complex, where we instead reacted **2** with methanol for around 12 h, giving pure **1** as the final product. NMR spectroscopic data were in agreement with the literature.[9]

Subjecting a $C_6D_6$ solution of **1** to an excess of $CO_2$ immediately set up two equilibria as shown in Scheme 2. The extent of reaction was readily followed by $^1$H NMR spectroscopy by observing either the OMe-peaks or the Cp* peaks. Compound **3** gives rise to two peaks of equal intensity in the MeO-region at 4.08 and 3.53 ppm, whereas **4** with its $C_{2v}$-symmetry gives a single peak slightly downfield from **3** at 3.54 ppm. As expected, adding more $CO_2$ shifted the equilibrium to the right but within the pressure limits of the NMR tube (ca 7 atm) the reaction could not be pushed fully to completion. Lower temperatures favoured the product formation, partly due to the higher solubility of $CO_2$.



**Scheme 1**



**Scheme 2**

Removing the $CO_2$ immediately shifted the equilibrium back to **1** and thus, compounds **3** and **4** were never isolated but were characterised in situ by $^{1}H$ and $^{13}C$ NMR spectroscopy (*cf.* the ESI). In addition to the MeO-peaks mentioned above, the $^{1}H\{^{13}C\}$ HMBC spectrum confirmed the correlation between the carbonyl carbon of **3** at 158.9 ppm and the methoxy protons at 3.53 ppm. Similarly for **4**, a correlation exists between the carbon peak at 159.2 ppm and the methoxy protons at 3.54 ppm.

To determine the equilibrium constant $K_1$, the ratio [**3**]/[**1**] was determined at different [$CO_2$] and temperatures as shown in Figure 1. A van´t Hoff plot (Figure S1) gave the enthalpy and entropy of reaction for the first equilibrium. The second equilibrium can only be observed with accuracy at higher [$CO_2$] and $K_2$ was therefore determined from [**4**]/[**3**] ratios at the highest possible carbon dioxide pressure at different temperatures (Figure S2). The thermodynamic data so obtained are given in Table 1. As expected both reactions are exothermic but entropically disfavoured.

The present equilibria are not rapid enough to give line broadening of the NMR signals and therefore we decided to study the rates of $CO_2$ insertion using magnetization transfer NMR spectroscopy, a technique that is useful when exchange rates are of the same order as the longitudinal relaxation.[18]

**Table 1.** Thermodynamic data for the two insertion equilibria in $C_6D_6$

| | $K^{293}/M^{-1}$ | $\Delta H°/kJmol^{-1}$ | $\Delta S°/JK^{-1}mol^{-1}$ |
|---|---|---|---|
| First equilibrium | 6.15±0.15 | –40.0±1.1 | –122±4 |
| Second equilibrium | 0.40±0.04[a] | –30.9±0.7 | –113±2 |

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[a] Determined from the van´t Hoff plot. Estimated standard deviation from the standard error of the thermodynamic data.

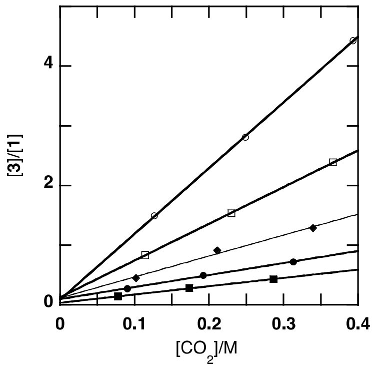

**Figure 1.** Conversion of the first equilibrium as a function of [$CO_2$] and temperature in $C_6D_6$. The solid lines denote the equation of a straight line fitted to data. ■ = 283 K, ● = 293 K, ◆ = 303 K, □ = 313 K, ❍= 323 K.

In an experiment, the $CH_3O$-peak of **1** at 4.00 ppm was selectively inverted and the intensities of the $CH_3O$-peaks of **3** and **4** were recorded as a function of pulse-mixing time. No significant perturbation of the $CH_3O$-peak of **4** could be detected and the reaction was treated as a two-site exchange between **1** and **3**. Experiments were performed at different [$CO_2$] and temperatures. The return of magnetization to equilibrium is governed by the exchange and relaxation rate constants for the two sites. Exchange rate constants are related by their populations and this model was fitted iteratively to the time dependent magnetization data using the software package CIFIT2.[11] Figure 2 shows an example of $^1$H-NMR intensities as a function of pulse mixing time and the corresponding fit. An exchange is always first order in the exchanging site and the exchange rate constants therefore correspond to the first order rate constants for the forward and reverse reaction of the first equilibrium, and are denoted $k_{obs}$ and $k_{-1}$, respectively.

A plot of $k_{obs}$ as a function of carbon dioxide concentration at different temperatures is given in Figure 3. This plot shows that the rate is first order in [$CO_2$]. Since the errors of the individual rate constants vary substantially, a weighted fit was used in some cases. On the other hand, the rate constant $k_{-1}$ was, as expected, independent of the carbon dioxide concentration. From Eyring plots (cf. Figure S3) activation parameters were calculated and these and the rate constants at room temperature are given in Table 2. All kinetic data are given in the Supporting Information.

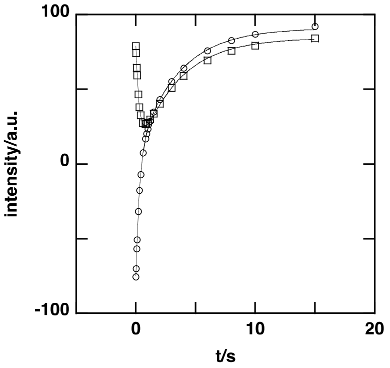

**Figure 2.** Intensity of the MeO-peaks of **1** (□) and **3** (○) as a function of pulse-mixing time after selectively inverting the peak of **1**. The solid lines are calculated values based on the fitted parameters from the program CIFIT2. [Zr] ≈ 13 mM. [$CO_2$] = 0.211 M. $T$= 303 K. See entry 5, Table S1.

**Table 2.** Kinetic data for the first insertion equilibrium

| | $k^{293\ a}$ | $\Delta H^{\ddagger}$/kJmol$^{-1}$ | $\Delta S^{\ddagger}$/JK$^{-1}$mol$^{-1}$ |
|---|---|---|---|
| $k_1$ | 3.20±0.12 $M^{-1}s^{-1}$ | 22±4 | -160±11 |
| $k_{-1}$ | 0.64±0.07 $s^{-1}$ | 61.5±2.2 | –39±7 |

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[a] The ratio of the rate constants gives a kinetic equilibrium constant of 5.0±0.6 $M^{-1}$, in good agreement, within standard deviation, with the value reported in Table 1.

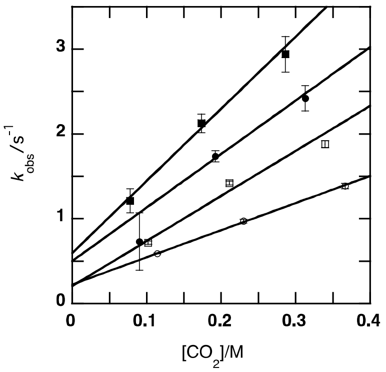

**Figure 3.** Observed first order rate constants in $C_6D_6$ for the forward reaction of the first equlibrium as a function of carbon dioxide concentration. The solid lines denote the equation of a straight line fitted to data. ❍ = 293 K, ☐ = 303 K, ● = 313 K, ■= 323 K.

Thus, the $CO_2$ insertion is first order in carbon dioxide and displays a highly negative activation entropy and a low activation enthalpy. The entropy contribution to the barrier at room temperature is approximately 70% and this indicates a closed transition state where the Zr–O bond is fairly intact.[19] A recent DFT calculation on the transition state of carbon dioxide insertion into a Zr-Me bond shows substantial interaction between the metal centre and the $CO_2$ oxygen but the present case is obviously different with the free electron pairs on the MeO-group.[20] Moreover, calculations on $d^0$ metal alkoxide insertions indicate a substantial interaction between the metal and carbon dioxide in the transition state.[3e] To gain a better picture of the current transition state we decided to model the insertions using density functional theory. For both insertions transition states were located and both of them have a clear, mainly electrostatic, interaction between the zirconium and the carbon dioxide oxygen in agreement with the closed transition state predicted by the observed activation parameters. The best approach vector for $CO_2$ is lateral, as depicted in Figure 4. The free energy barrier for the first insertion is 59 kJ/mol. The barrier is mostly entropic in character, in good agreement with the experiments. The gas phase enthalpy of addition is only ca. 3 kJ/mol. The distances from Zr to the two methoxy oxygens differ by only 0.15 Å, corroborating our assumption that the reacting Zr-*O*Me bond is fairly intact in the transition state.

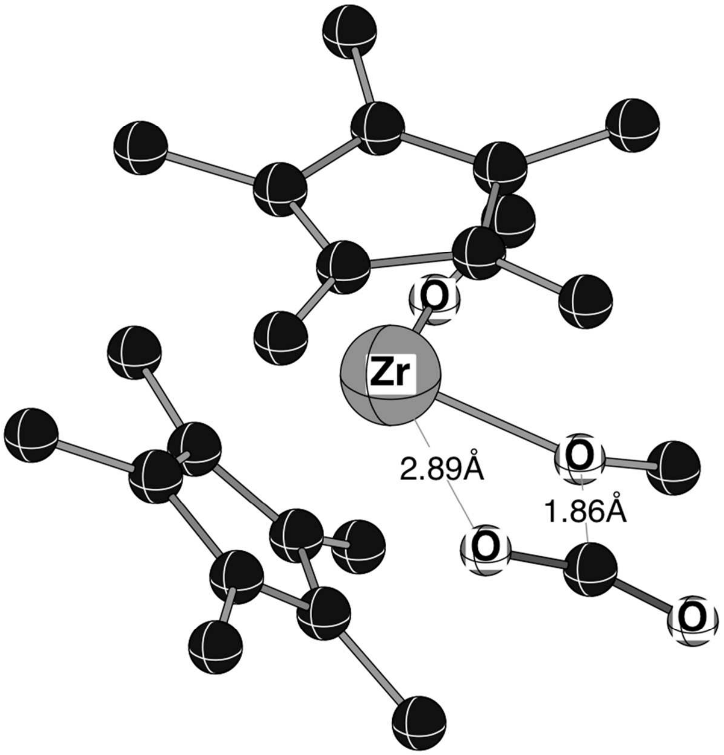

**Figure 4.** Calculated transition state for the first insertion. Hydrogen atoms are omitted for clarity.

The intermediate is virtually isoergic with the starting materials, but there is strong enthalpy-entropy compensation. The reverse reaction, liberating $CO_2$ from the intermediate, includes significant bond breaking. The backwards reaction also has a calculated free energy barrier of 59 kJ/mol, but here the gas phase enthalpy contributes 52 kJ/mol of the total. The higher enthalpic contribution of the reverse reaction is again in good agreement with the experimental results. The second insertion is very similar to the first, but is now calculated to be slightly endergonic. The forward barrier is 56 kJ/mol, mostly entropic, and the backwards barrier is 53 kJ/mol, mostly enthalpic.

Comparing the rate of insertion to other similar systems the present rate is around 25 times higher than that reported for $Nb(OEt)_5$, at 0.12 $M^{-1}s^{-1}$.[3d] Insertion into tin-alkoxides, another prominent homogeneous alcohol carboxylation catalyst, is also reported to be slower, taking around 30 min to reach equilibrium for $Bu_3SnOMe$.[3b] Compound **1** also has the advantage over less ligated metal-alkoxides in that there is no dimerization, a process that often confines much of the catalyst in a less active form. The reported lack of reactivity of the corresponding Cp-complex indicates that there is a substantial ligand effect in this type of reaction as has been observed previously for zirconocene mediated activations of small molecules.[7,21] In relation to $ZrO_2$ catalysed DMC formation the current findings support the proposal that insertion of $CO_2$ into a terminal Zr-OMe bond is a key step.[4]

In conclusion we report a fast and reversible insertion of $CO_2$ into O-alkyl bonds of a neutral zirconocene. The forward reaction is bimolecular and has a very closed transition state with little bond breaking. Rates of insertion are the highest reported for an early transition metal which holds promise for the development of efficient alcohol carboxylation catalyst. Work towards this end is ongoing.

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