Chemical Interconversions in the System Tp*Zn/CO_2/Alcohol [Tp* = Substituted Tris(pyrazolyl)borate]☆

Michael Ruf, Friedrich Alexander Schell, Rainer Walz, and Heinrich Vahrenkamp*

Institut für Anorganische und Analytische Chemie der Universität Freiburg,
Albertstraße 21, D-79104 Freiburg, Germany

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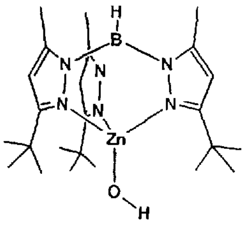
The zinc hydroxide complexes Tp*Zn–OH with $Tp^{Cum,Me}$ = tris(3-cumenyl-5-methylpyrazolyl)borate and $Tp^{tBu,Me}$ = tris(3-tert-butyl-5-methylpyrazolyl)borate can be converted to the alkyl carbonate complexes Tp*Zn–OCOOR by reaction with dialkyl dicarbonates or with alcohol and CO_2. An alternative formation reaction is the treatment of the pyrazolyl borate with zinc perchlorate and potassium carbonate in alcohol. The interconversion between $Tp^{Cum,Me}$Zn–OH and $Tp^{Cum,Me}$Zn–OCOOMe in methanol-containing solution can be repeatedly performed in both directions by bubbling either CO_2 or N_2 through the solution. The alkyl carbonate complexes show a variable sensitivity towards hydrolytic destruction with reformation of the hydroxide complexes. The complexes $Tp^{tBu,Me}$Zn–OCOOR (R = Me, Et) release CO_2 under high vacuum to form the alkoxide complexes $Tp^{tBu,Me}$-Zn–OR, which could not be obtained pure due to their extreme water sensitivity. Indirect evidence for their existence is also obtained by the reaction between $Tp^{Cum,Me}$Zn–OCOOMe and methyl iodide, forming $Tp^{Cum,Me}$Zn–I and dimethyl ether. The zinc hydroxide complexes catalyse the formation of diethyl carbonate from ethanol and CO_2.

It is a challenging task of modern chemistry to make use of carbon dioxide as a feedstock. Various approaches to this have been discussed, most of which require catalytic activation by metal complexes[1–8]. Among them is the conversion of alcohols to dialkyl carbonates that could serve as starting materials for industrial organic syntheses. Numerous patents exist for this process[9]. Almost all of them require catalysis of the CO_2/ROH reaction by Lewis acidic metal compounds, but to our knowledge the process has not yet reached the state of industrial applicability.

The biological equivalent of this system for hydrolytic CO_2 activation is the carbonic anhydrase group of enzymes[10]. These catalyse the equilibration between carbon dioxide/water and bicarbonate, and the Lewis acidic metal ion in the enzyme is zinc. Unlike the formation of dialkyl carbonates, which is quite endothermic, the reversible formation of hydrogen carbonate ("bicarbonate") is thermodynamically feasible.

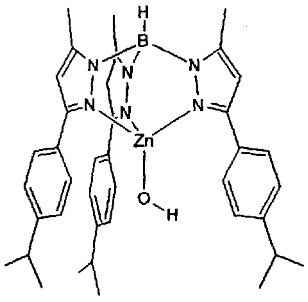
Our contribution to this field of chemistry has been the design of hydrolytically active zinc complexes that can model the enzyme's reactions. Specifically, the pyrazolyl borate complexes **1a**[11] and **1b**[12] were found to be powerful nucleophiles. They not only cleave esters, amides and phosphates[13,14], but they also incorporate CO_2, leading, depending on the conditions, to the formation of zinc bicarbonate, carbonate, or alkyl carbonate complexes, respectively[11,12]. Previously we had not probed the reactivity of the resulting complexes nor the possible use of **1a** and **1b** for catalytic conversions.

This paper reports our chemical findings for the reaction system Tp*Zn–OH/CO_2/alcohol for stoichiometric as well as catalytic reactions. The investigations have as their focal point zinc-alkyl carbonate complexes as key intermediates. Such intermediates are generally accepted to be involved in Zn-catalysed reactions between epoxides and CO_2[8]. To our knowledge the only previous study on their chemistry is that by Kato and Ito[15] on the interconversions between methoxide and methyl carbonate complexes of the [15]aneN_4 · Zn unit.



$Tp^{tBu,Me}$Zn-OH

1a



$Tp^{Cum,Me}$Zn-OH

1b

Alkyl Carbonate Complexes

We had observed previously[11] that **1a** is converted to the dialkyl carbonate complexes **2a** and **3a** by prolonged reaction with the neat dialkyl dicarbonates. We have now found that this conversion is limited to these two cases for **1a** and does not work for instance with di(*tert*-butyl)dicarbonate. On the other hand we had found[12,13] that **1b** is a stronger nucleophile than **1a**. This could be verified here by combining stoichiometric amounts of **1b** and dimethyldicarbonate (MeOCOOCOOMe) in dichloromethane, leading to immediate formation of **2b**.

$Tp^{tBu,Me}Zn{-}OCOOR$ $Tp^{Cum,Me}Zn{-}OCOOR$
2a: R = Me **2b**: R = Me
3a: R = Et **3b**: R = Et

2b and **3b** had also been obtained before by CO_2 absorption in alcoholic solutions of **1b**[12]. This reaction, which does not work for **1a**, is another demonstration of the higher reactivity of **1b**. It is limited too, however. We found that it does not work when *tert*-butyl alcohol or benzyl alcohol is used. Alternatively **2b** was obtained from the pyrazolyl borate, zinc perchlorate, methanol, and potassium carbonate in dichloromethane. Thus three ways of combining an alcohol and CO_2 in the ligand sphere of zinc have been found, of which one uses CO_2 directly while the other two require previous incorporation of CO_2 in the precursor compounds carbonate or dialkyldicarbonate, respectively.

Elimination of CO_2

The ease of incorporation of CO_2 to form **2b** and **3b** and the good accessibility of all four complexes **2** and **3** raised the question of whether it would be easy to eliminate CO_2 from them. Here, too, we had gained some previous experience with complexes **2a** and **3a**[11]. Both these complexes are very sensitive towards traces of water, being immediately converted to the starting complex **1a**. In contrast, methanolic solutions of **1b** not only pick up CO_2 from the normal atmosphere to form **2b**[12], but they incorporate CO_2 even in methanol with up to 20% water. In accordance with this, aqueous hydrolysis of **2b** in nonprotic solvents requires activation by heat or ultrasound. The reason for the vastly differing reactivities of all complexes **a** and **b** must be the encapsulation of the functional ligand in the pocket of the cumenyl substituents of the $Tp^{Cum,Me}$ ligand.

Nevertheless it could be shown for **1b** and **2b** that the CO_2 uptake is an equilibrium reaction that can easily be reversed. This was demonstrated in an NMR experiment in $CDCl_3$ solution under strictly anhydrous conditions. While **1b** alone did not absorb CO_2, a stoichiometric mixture of **1b** and methanol did. The resulting solution of **2b** was reconverted to **1b** in a stream of N_2, and this absorption/elimination sequence could be performed repeatedly. This shows that the equilibrium conditions favour neither the insertion product **2b** nor the elimination product **1b**.

The weak fixation of CO_2 in **2b** is also emphasized by the fact that treatment of **2b** with methyl iodide does not lead to dimethyl carbonate. CO_2 elimination must be invoked in order to explain why dimethyl ether is formed instead together with the Zn–I complex **4b**. The reaction conditions for CO_2 elimination under the influence of N_2 and CH_3I are similar, and one possible explanation for the course of the CH_3I reaction is the intermediate formation of **1b** due to the presence of traces of water. This could not be verified, however: care was taken to avoid water, and **1b** was found not to react with CO_2 in the absence of methanol. Alternatively, one could assume that the methoxide complex $Tp^{Cum,Me}Zn{-}OMe$ is an intermediate in this reaction. We have, however, no evidence for its formation.

In contrast, we had previously observed that CO_2 elimination from **3a** requires a very high vacuum and high temperatures, and that the resulting complex **6a** is so labile that it could not be isolated in a pure form[11]. This was reaffirmed in the present study by thermolysis of **2a** at 10^{-5} mbar, resulting in impure **5a**. **5a** is so sensitive towards hydrolysis that attempted recrystallization yielded only **1a**.

$Tp^{Cum,Me}Zn{-}I$ $Tp^{tBu,Me}Zn{-}OR$
4b **5a**: R = Me
6a: R = Et

The CO_2 elimination studies established the interrelation of the Zn–OH, Zn–OR, and Zn–OCOOR species. It is worth mentioning that no evidence for a Zn–OCOOH species was found in the $Tp^{Cum,Me}Zn$ system, whereas there was good evidence for it in the $Tp^{tBu,Me}Zn$ system[11]. Thus the latter seems to be the better candidate for the modelling of carbonic anhydrase reactivity, whereas the former promises applicability for zinc-supported CO_2/alcohol reactions.

Zinc-Mediated Formation of Diethyl Carbonate

The alkyl carbonate complexes accessible from **1b**, alcohol, and CO_2 mark the half-way point in the conversion of CO_2 to dialkyl carbonates. Although their formation is obviously thermodynamically feasible, the complete reaction (1) is not, due mostly to the unfavourable formation of water from the alcohols[9].

$$CO_2 + 2\,ROH \rightarrow CO(OR)_2 + H_2O \qquad (1)$$

Attempts to convert alcohols to dialkyl carbonates therefore not only have to meet the challenge of catalytically overcoming the inertia of carbon dioxide but also to provide a means of enforcing the endothermic reaction. A popular indirect way of doing this is the use of ethylene carbonate (accessible from ethylene oxide and CO_2) as an intermediate[8,16,17]; reactions between this and alcohols yield dialkyl carbonates, at the expense, however, of coproducing ethylene glycol. The preferable direct route requires the discovery of suitable water-consuming reagents and catalysts. Typical catalysts that have been used for the synthesis of diethyl carbonate are alkoxides of thallium[18] and tin[9,19]. But even after optimizing the reaction conditions the turnover numbers could not be increased much over 2 moles of product per mole of catalyst. This means that there is a yet no technical production of dialkyl carbonates from CO_2 and alcohols, and noncatalytic procedures, i.e. reactions between ROH, R′Hal, CO_2, and base are discussed as alternatives[20,21].

We tested the catalytic efficiency of complexes **1a** and **1b** for the synthesis of diethyl carbonate. After extensive optimization the following reaction conditions were found best: temperature 150°C; pressure 110 bar; reaction time 20 h. The reactions were performed with 25 ml of ethanol in a 250-ml autoclave; 1 mmol of catalyst was dissolved in the ethanol; 20 g of 4-Å molecular sieve, held in a container above the reaction solution, was used as water-absorbing reagent. Qualitative and quantitative product analysis was performed by GC. Under these conditions the reaction solution might be in the supercritical state, which was found to be favourable for zinc-catalysed copolymerizations of epoxides and CO_2[22]. Although we were not able to determine the critical data of the specific mixture, the presence of solvent in the container of the drying agent after the reaction indicates a supercritical state.

Under all conditions the yields of diethyl carbonate were low, the maximum total turnover numbers per experiment being around 0.3. Two side products were observed: one of them was acetaldehyde diethyl acetal, resulting from oxidation of the ethanol; the other was diethyl ether, resulting from catalytic dehydration of ethanol. Despite these unfavourable findings the catalytic activity of complexes **1** is undoubtable, because in the absence of **1a** or **1b** no reaction took place. Furthermore the use of the corresponding chloride complexes Tp*Zn–Cl was nonproductive, proving that the Zn–OH function is the centre of reactivity as observed above.

Variations of the drying agent, e.g. using $MgSO_4$, $CaCl_2$, CaO, or P_2O_5, reduced the yield of diethyl carbonate dramatically. The addition of bases, specifically sodium ethoxide, improved the situation. Runs with 1 equivalent of NaOEt per equivalent of catalyst yielded turnover numbers (TON) for diethylcarbonate production of 0.34 for **1a** and 2.0 for **1b**, whereas NaOEt alone did not catalyse the reaction. Thus the reaction yields of the patented catalyst systems could be reached, and **1b** was once again found to be more active than **1a**.

In summary it can be stated that the pyrazolylborate–zinc-hydroxide complexes have some potential for the activation of carbon dioxide. They allow stoichiometric uptake of CO_2 and they can mediate synthetically useful CO_2 conversions. Their key feature, as in other reactions, is their highly nucleophilic Zn–OH function. It remains to be seen whether an improved design of the pyrazolylborate ligands can further improve this property, thereby increasing their reactivity in stoichiometric as well as catalytic interconversions.

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Experimental Section

The general working and measuring methods are described in ref.[23]. Complexes **1a**[11] and **1b**[12] were prepared as described. The alcohols used were water-free. The CO_2 was of 99.995% purity.

Synthesis of **2b**. – (a) *From Dimethyl Dicarbonate:* 200 mg (0.29 mmol) of **1b** in 20 ml of dichloromethane was treated with 31 µl (39 mg, 0.29 mmol) of dimethyl dicarbonate, and the solution was stirred for 30 min. All volatiles were removed in vacuo. The product was washed with 10 ml of methanol and dried in vacuo, resulting in 195 mg (90%) of colourless **2b**[12].

(b) *From Methanol and Potassium Carbonate:* 2.00 g (3.08 mmol) of $KTp^{Cum,Me}$[12] in 50 ml of dichloromethane was treated with stirring with a solution of 1.15 g (3.09 mmol) of $Zn(ClO_4)_2 \cdot 6\,H_2O$ in 10 ml of methanol, upon which a colourless precipitate was formed. After addition of a solution of 0.42 g (3.08 mmol) of K_2CO_3 in 10 ml of methanol, the mixture was stirred for 15 h. Then the precipitate (now mostly $KClO_4$) was filtered off, and the volume of the solution was reduced in vacuo to one third. A colourless precipitate was slowly formed, which was filtered off and dried in vacuo, leaving behind 1.50 g (65%) of **2b**[12].

Hydrolysis of **2b**. – (a) When small amounts of water were added to methanolic solutions of **2b** the spectra indicated that the methyl carbonate ligand was not affected. Only after addition of more than 20% of water and prolonged reaction times did uncontrolled hydrolysis set in.

(b) A drop of D_2O was added to a solution of 0.05 g of **2b** in 3 ml of $CDCl_3$. Vigorous shaking did not result in destruction of **2b**. Only after the mixture had been heated to reflux for a few minutes or had been exposed to ultrasound could the conversion to **1b** and methanol be observed by ^1H NMR.

Reversible CO_2 Uptake by **1b**: 0.01 g of **1b** were dissolved in 0.5 ml of $CDCl_3$ in an NMR tube under strict exclusion of air and water. Bubbling CO_2 through this solution did not lead to any spectral changes. After addition of a stoichiometric amount of methanol its ^1H-NMR signal at $\delta = 3.35$ was observed. Bubbling CO_2 through the solution caused this signal to disappear and be replaced by that of **2b** at $\delta = 2.42$. Subsequent bubbling of N_2 through the solution reversed this reaction. The CO_2/N_2 cycle was repeated four times, each time taking 10 min per gas. The $CDCl_3$ lost through evaporation was replaced to enable quantitative NMR measurements. **1b** and **2b** were the only observable chemical species and their quantity was found not to decrease.

4b: 200 mg (0.27 mmol) of **2b** and 17 µl (38 mg, 0.27 mmol) of CH_3I in 30 ml of dichloromethane were stirred for 1 h. After this time the ^1H-NMR resonance of dimethyl ether at $\delta = 2.85$ was observed. 20 ml of methanol was added, and the volume of the solution was reduced to one half in vacuo. Slow precipitation yielded 190 mg (89%) of colourless crystalline **4b**, m.p. 216°C, which was filtered off and dried in vacuo. – IR (KBr, cm^{-1}): $\tilde{\nu} = 2531$ w (BH), 1518 s, 1437 s (pyrazole). – ^1H NMR ($CDCl_3$): $\delta = 1.27$ (d, $J = 6.9$ Hz, 18H, CH_3-*i*Pr), 2.55 (s, 9H, CH_3-pyrazole), 2.93 (sept., $J = 6.9$ Hz, 3H, CH-*i*Pr), 6.16 (s, 3H, H-pyrazole), 7.24 (d, $J = 8.2$ Hz, 6H, Ph-3 and Ph-5), 7.57 (d, $J = 8.2$ Hz, 6H, Ph-2 and Ph-6). – $C_{39}H_{46}BIN_6Zn$ (801.9). calcd. C 58.41, H 5.78, N 10.48; found C 58.15, H 5.77, N 10.40.

5a: 10.0 mg (0.018 mmol) of **2a** in an NMR tube were placed in a Schlenk tube attached to a diffusion pump. The tube was evacuated to $7 \cdot 10^{-6}$ mbar for 12 h, after which time **2a** was unchanged according to ^1H NMR. When the sample was slowly heated to 150°C under the same vacuum, a subsequent ^1H-NMR spectrum (in $CDCl_3$) showed signals at $\delta = 1.41$ (s, 27H, *t*-Bu), 2.37 (s, 9H, Me), 4.05 (s, 3H, OMe), and 5.78 (s, 3H, H-pyrazole) besides minor signals attributable to **2a** and decomposition products. The four signals can be assigned to **5a** in accordance with those assigned to **6a**[11]. Attempts to isolate pure **5a** by recrystallization (from $CDCl_3$ or benzene) were met with failure because hydrolysis of **5a** to **1a** could not be avoided. Attempts to perform the pyrolysis of **2a** with larger quantities led to increased amounts of side products, thereby preventing the formation of pure **5a**.

Catalytic Synthesis of Diethyl Carbonate: Reactions were performed in a 250-ml autoclave (Roth, Karlsruhe) equipped with inlet and outlet valves and a manometer. All manipulations were carried out with carefully dried reagents and apparatus. The autoclave was charged with 25 ml of ethanol, 1 mmol of catalyst or 1 mmol of catalyst plus 1 mmol of NaOEt, and 20 g of 4-Å molecular sieve (1.6–2.5-mm size, Roth, Karlsruhe) held in a glass beaker above the liquid phase. CO_2 was pumped into the autoclave, which was then placed in its oven. After the run and cooling to room temperature, the CO_2 was vented off. The reaction mixture was distilled to dryness. The distillate was analysed in a gas chromatograph (Chrompack CP 9001) equipped with a 25-m CP-WAX-52 CB column that had previously been calibrated for the reaction products ethanol, diethyl carbonate, diethyl ether, and acetaldehyde diethyl acetal. The turnover number (moles of product per mole of catalyst) was calculated from the amount of diethyl carbonate. Runs with 1 mmol of NaOEt in the absence of a zinc complex did not yield any diethyl carbonate.

During the optimization process the reaction time was varied between 5 h and 3 d, the temperature between 80 and 200°C, and the pressure between 50 and 180 bar. The best yields were found for a reaction time of 20 h at 150°C and 100 bar, which corresponds to charging the autoclave with 55 g of CO_2. Table 1 lists the product yields for these reaction conditions.

Table 1. Details of the catalytic diethyl carbonate syntheses

Catalyst (1 mmol each)	turnover EtOH (%)	Yields DEC[a] (mmol)	Et$_2$O (mmol)	ADA[a] (mmol)
1a	0.96	0.24	0.42	2.17
1b	0.90	0.33	1.13	0.66
$Tp^{tBu,Me}Zn{-}Cl$	1.30	0.00	0.73	4.19
$Tp^{Cum,Me}Zn{-}Cl$	0.40	0.00	0.73	0.33
1a + NaOEt	1.01	0.34	1.20	2.52
1b + NaOEt	0.78	2.01	0.05	0.98

[a] DEC = diethyl carbonate; ADA = acetaldehyde diethyl acetal.

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☆ Dedicated to Prof. *Walter Siebert* on the occasion of his 60th birthday.