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Pyrazolylborate–Zinc Alkoxide Complexes. 1. Basic Properties, Methylations, and Heterocumulene Insertions

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While a solution of $Tp^{Ph,Me}Zn–OH$ in methanol contains only traces of $Tp^{Ph,Me}Zn–OMe$, according to the equilibrium constant $K = 5.8 \times 10^{-4}$, the reactions of $Tp^{Ph,Me}Zn–OH$ with the electronegative alcohols trifluoroethanol and hexafluoro-2-propanol easily yield $Tp^{Ph,Me}Zn–OCH_2CF_3$ and $Tp^{Ph,Me}Zn–OCH(CF_3)_2$. The extremely hydrolytically sensitive $Tp^{Ph,Me}Zn–OR$ complexes, with R = Me, Et, i-Pr, and CH_2CH_2F, as well as $Tp^{Cum,Me}Zn–OR$, with R = Me and i-Pr, are accessible from the Tp*Zn–hydride complexes and the corresponding alcohol. Alkylations with methyl iodide have revealed the high nucleophilicity of $Tp^{Ph,Me}Zn–OMe$ by conversion to dimethyl ether and $Tp^{Ph,Me}Zn–I$. This conversion occurs rapidly not only with pure $Tp^{Ph,Me}Zn–OMe$ but also with $Tp^{Ph,Me}Zn–OH$ (as such or in the presence of methanol) and with $Tp^{Ph,Me}Zn–OCOOMe$. A relation of the Tp*Zn–alkoxides to the function of the zinc enzyme alcoholdehydrogenase exists in the reaction of $Tp^{Ph,Me}Zn–OCH(CH_3)_2$ with aromatic aldehydes, which yields acetone and the corresponding benzyl oxides $Tp^{Ph,Me}Zn–OH_2Ar$. The heterocumulenes carbon dioxide, carbon disulfide, isothiocyanates, and one isocyanate are inserted into the Zn–OR bonds, yielding one alkyl carbonate complex ($Tp^{Ph,Me}Zn–OC(O)OMe$), two xanthogenate complexes ($Tp^{Ph,Me}Zn–SC(S)OR$), three iminothiocarbonate complexes ($Tp^{Ph,Me}Zn–SC(NR')OR$), and one alkyl carbamate complex ($Tp^{Ph,Me}Zn–NR–COOMe$). All insertion reactions can be described by a common mechanism involving a four-center intermediate in which the most basic heteroatom of the heterocumulene is attached to zinc.

Introduction

The motivation for the work presented in this and the two following papers[1,2] was 2-fold. First, it was part of our continuing attempts to model the structure and function of the zinc enzymes alcoholdehydrogenase[3−5] and carbonic anhydrase.[6−8] Second, it resulted from the idea that a Zn−OR function encapsulated in the hydrophobic environment of a highly substituted pyrazolylborate ligand should be at least as potent a nucleophile as the Zn−OH function. Therefore, a rich chemistry of Tp*Zn−OR complexes could be expected which should be similar to but characteristically different from that of the Tp*Zn−OH complexes.[8−12] In the course of the work described here, it turned out that following the line of alcoholdehydrogenase modeling was unproductive, i.e., a substantial activation of the C−H bonds of the $Zn-O-CH_2-R$ unit toward hydride abstraction could not be achieved.[13] However, this failure was more than compensated by our findings on the reactivity of the Zn−OR function.

Monomeric zinc alkoxides, like the alkoxides of other metals, are rare.[14,15] Their tendency for OR bridging must

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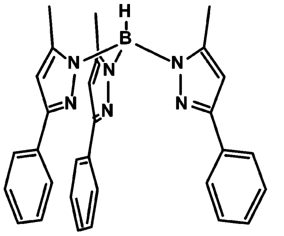
be suppressed either by the formation of negatively charged complexes or by the steric bulk of the alkoxides themselves or their coligands. Typical coligands for this purpose are the multidentate N and S chelators. But even with their assistance only five structurally characterized Zn−OR complexes with terminal nonchelating alkoxide ligands, which do not belong to the pyrazolylborate−zinc alkoxide family, have been found until today.[16−20]

The favorable properties of the highly substituted tris(pyrazolyl)borate ligands, Tp*, which allow the easy handling of monomeric Zn−H,[11,21] Zn−R,[11,21] Zn−OH,[10,11] and even Zn−SH[22] complexes, made us expect that they would also offer an entry to the preparative chemistry of monomeric zinc alkoxides Tp*Zn−OR. This was borne out early on when we found that the thermolysis of alkyl carbonates Tp*Zn−OCOOR affords the alkoxides Tp*Zn−OR.[6] But during these studies we also learned that these alkoxides are extremely sensitive to moisture, reverting to Tp*Zn−OH. Lacking the necessary equipment in those days, we refrained from studying their chemistry further.

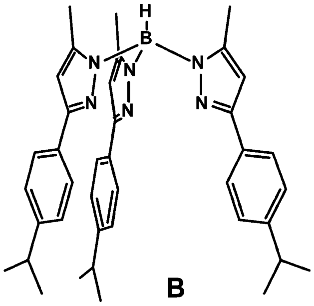
In recent years the attempts to model the zinc enzyme alcoholdehydrogenase have revitalized the interest in Tp*Zn−OR complexes. We found that they are accessible from Tp*Zn−OH and HOR and that they are easier to handle when the alkoxide group R is more electronegative, e.g., R = OCH_2CF_3, OCH_2CCl_3 or $OCH_2C_6F_5$.[3] Parkin found that even the Tp*Zn−OR complexes derived from methanol, ethanol, etc. exist in equilibrium with Tp*Zn−OH in alcoholic solutions, albeit in very small concentrations,[23,24] and recently an attempt to recrystallize $Tp^{Ph,Me}$Zn−OH[25] from methanol accidentally led to $Tp^{Ph,Me}$Zn−OMe.[26] As of today, a total of six structures of Tp*Zn−OR complexes have been reported, surpassing the number of structures for Zn−OR complexes with non-Tp ligands and thereby underlining the advantages of the Tp* ligands for the stabilization of labile, functional, and low-coordinate zinc species.

The purported analogy between the Tp*Zn−OH and Tp*Zn−OR complexes allowed the prediction that the OR function would be not only a potent nucleophile but also a very good leaving group. Thus, two characteristic reaction types could be envisaged: (i) alkylation with release of the alkylation product, i.e., a dialkyl ether, and (ii) insertion of carbon dioxide into the Zn−OR bond with formation of an alkyl carbonate complex. The latter would provide a new variant of the modeling of carbonic anhydrase which Parkin[27,28] and ourselves[6−8] had studied with the Tp*Zn−OH complexes previously. Yet while the primary insertion products of CO_2 and other heterocumulenes into the Zn−OH bond, e.g., a Tp*Zn−OCOOH complex, could not be isoleted due to follow-up reactions,[6,7] their alkylated derivatives resulting from insertion into the Zn−OR bond, e.g., Tp*Zn−OCOOR complexes, should be isolable.

Thus, it seemed attractive to study the reactivity of pyrazolylborate−zinc alkoxides. Yet prior to our own work described in this and the two succeeding papers, only Parkin's equilibrium studies[23,24] and his and our attempts to model alcohol dehydrogenation[3,4,23,29] had been reported. We therefore installed the necessary inert atmosphere techniques and set out to exploit the Tp*Zn−OR chemistry. This paper represents the basic properties. The succeeding papers report the solvolytic chemistry[1] and acid−base reactions[2] of the Tp*Zn−OR complexes. All Tp*Zn complexes in this series are derived from $Tp^{Ph,Me}$ (**A**) and $Tp^{Cum,Me}$ (**B**).



A



B

Results and Discussion

Preparations. The proposals put forth for the activation of alcohols by the zinc enzyme alcoholdehydrogenase involve their attachment to zinc as alkoxides.[30] The model studies of our competitors[17,20,23] and ourselves[3,4,6] have shown, however, that in the presence of water (and in the absence of additional stabilizing features) the Zn−OH or Zn−OH_2 complexes are highly preferred over the Zn−OR complexes. One of the factors responsible for this[24] rests in the fact that the pK_a values of the aliphatic alcohols, e.g., methanol (15.5) or 2-propanol (17.0), are higher than that of water.[31] Accordingly, we found it easy to convert Tp*Zn−OH to Tp*Zn−OR with the more acidic alcohols CF_3CH_2OH, CCl_3CH_2OH, $C_6F_5CH_2OH$, and *p*-NO_2-$C_6CH_4CH_2OH$.[3] We could now extend the list of such reactions by treating $Tp^{Ph,Me}$Zn−OH with trifluoroethanol and hexafluoro-2-propanol. Reactions in dichloromethane produced the fluoroalkoxide complexes **1** and **2**, which are sufficiently stable against hydrolysis that they can be handled in the normal atmosphere.

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$Tp^{Ph,Me}Zn\text{-}OCH_2CF_3$ **1** $Tp^{Ph,Me}Zn\text{-}OCH(CF_3)_2$ **2**

While the isolation of the simple alkoxides, Tp*Zn−OMe, Tp*Zn−OEt, etc., from the Tp*Zn−OH/ROH reactions seems impossible,[3,23,26] it could still be shown that they exist as equilibrium components in very small quantities in Tp*Zn−OH/ROH mixtures.[23,24] The accidental observation that a methanol solvate of $Tp^{Ph,Me}Zn{-}OMe$ crystallized from solutions of $Tp^{Ph,Me}Zn{-}OH$ in anhydrous methanol[26] made us assume that this special alkoxide might be present as a more prominent constituent of the equilibrium mixture. We therefore determined the equilibrium constant for reaction 1.

$$Tp^{Ph,Me}Zn{-}OH + MeOH \rightleftharpoons Tp^{Ph,Me}Zn{-}OMe + H_2O \quad (1)$$

The obtained value of K is 5.8×10^{-4}; i.e., the equilibrium concentration of $Tp^{Ph,Me}Zn{-}OMe$ is again very small. Parkin observed $K = 1.4 \times 10^{-3}$ for the corresponding reaction of $Tp^{tBu,Me}Zn{-}OH$ with methanol, which is roughly the same order of magnitude.[23] Both equilibrium constants underline the unequivocal preference of the Tp*Zn−OH species and the nonexistence of pyrazolylborate−zinc alkoxides in an aqueous environment.

While it thus was obvious that this is no productive entry to the chemistry of the pyrazolylborate−zinc alkoxides, Parkin had already demonstrated that this entry is possible via the alcoholysis of $Tp^{tBu,Me}Zn$−hydride.[23,32] We could verify this by using the hydrides $Tp^{Ph,Me}Zn{-}H$[33] and $Tp^{Cum,Me}Zn{-}H$, which we prepared by the Kläui method[34] from the corresponding fluorides with triethylsilane. Both hydrides were reacted with aliphatic alcohols at elevated temperatures in toluene solutions. $Tp^{Ph,Me}Zn{-}H$ and methanol, ethanol, 2-propanol, and 2-fluoroethanol yielded complexes **3**−**6**, and $Tp^{Cum,Me}Zn{-}H$ and methanol as well as 2-propanol yielded complexes **7** and **8**. The synthesis and handling of the alkoxides requires strictly anhydrous conditions, i.e., glovebox techniques. All alkoxides **1**−**8** are colorless powders, melting above 200 °C without decomposition.

$Tp^{Ph,Me}Zn\text{-}OR$
3: R = Me
4: R = Et
5: R = i-Pr
6: R = CH_2CH_2F

$Tp^{Cum,Me}Zn\text{-}OR$
7: R = Me
8. R = i-Pr

Characterization. While the IR spectra of the new complexes show no characteristic feature other than the BH stretching vibration, in the ^1H NMR spectra the resonance for the $O{-}CHX_2$ unit occurs in the typical range around 3.5−4 ppm, and the ^{13}C NMR signals of the alkoxide units appear in the characteristic range of 55−65 ppm, which has been observed before.[3,23] The simplest of the alkoxide complexes, **3**, was chosen for structure determination. Figure 1 shows that the zinc ion in **3** is in a rather symmetrical pseudotetrahedral ZnN_3O coordination with N−Zn−N angles between 92° and 96°, N−Zn−O angles between 119° and 125°, and a Zn−O bond length of 1.843(2) Å, which is midway in the range observed for the other pyrazolylborate−zinc alkoxides (1.81−1.87 Å).[3,23,26]

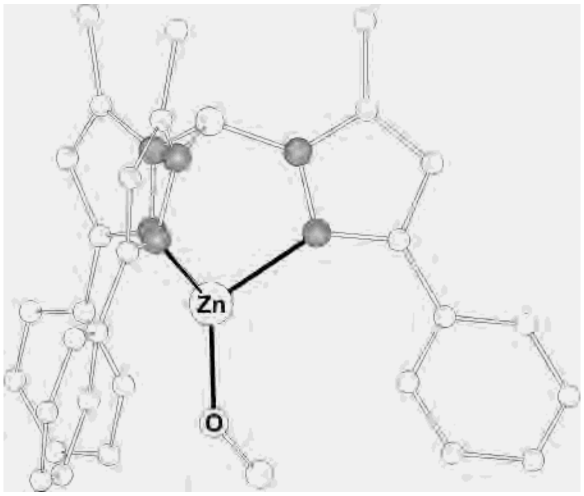

Figure 1. Molecular structure of $Tp^{Ph,Me}Zn{-}OMe$ (**3**).

Methylations. To demonstrate the high nucleophilicity of the zinc-bound alkoxides, we chose a reaction that we had studied in detail for the homologous thiolates $Tp^{Ph,Me}Zn{-}SR$,[35] the removal of the chalcogenolate function by alkylation with methyl iodide. Indeed, complexes **3** and **4** reacted with methyl iodide in $CDCl_3$ according to eq 2.

$$Tp^{Ph,Me}Zn{-}OR + MeI \rightarrow Tp^{Ph,Me}Zn{-}I + Me{-}O{-}R \quad (2)$$

The mechanistic interpretation of this reaction, like that of $Tp^{Ph,Me}Zn{-}SR$ with methyl iodide,[35] involves the intermediate formation of a cationic Zn(MeOR) complex in which the hard and uncharged ether ligand is labile and easily replaced by iodide, resulting in the stable Zn−I complex.

The methyl iodide reactions of **3** and **4** were so facile that they induced us to test the reaction of $Tp^{Ph,Me}Zn{-}OH$ with methyl iodide. This reaction also proceeded smoothly to produce $Tp^{Ph,Me}Zn{-}I$. But from it resulted not only the expected organic product methanol but also a considerable amount of dimethyl ether. To explain this one must assume the presence of $Tp^{Ph,Me}Zn{-}OMe$ (**3**) in the reaction mixture. Yet, as shown above, **3** exists only in negligible quantities in mixtures of $Tp^{Ph,Me}Zn{-}OH$ and methanol. Hence, to generate the observed amounts of dimethyl ether, the nucleophilicity of **3** must exceed that of $Tp^{Ph,Me}Zn{-}OH$ by far.

A further indication that this is so was then found in the methyl iodide reaction of the alkyl carbonate complex

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$\mathrm{Tp^{Ph,Me}Zn{-}OCOOMe}$ (**10**, see below). We had already observed that the analogous complex $\mathrm{Tp^{Cum,Me}Zn{-}OCOOMe}$ forms from $\mathrm{Tp^{Cum,Me}Zn{-}OH}$ and an excess of CO_2 in methanol[8,36] and that purging the reaction solution with nitrogen reverts it to $\mathrm{Tp^{Cum,Me}Zn{-}OH}$. On the basis of these previous observations and the ones made here, we could expect that solutions of $\mathrm{Tp^{Ph,Me}Zn{-}OCOOMe}$ contain a certain amount of $\mathrm{Tp^{Ph,Me}Zn{-}OMe}$ (**3**) or, if traces of water are present, also $\mathrm{Tp^{Ph,Me}Zn{-}OH}$ and methanol. In such a mixture **3** could be expected to be quickly consumed by reaction with methyl iodide, thereby enforcing its continued formation from $\mathrm{Tp^{Ph,Me}Zn{-}OCOOMe}$, which would lead to the complete consumption of the methyl carbonate complex. Exactly this was observed. Treatment of $\mathrm{Tp^{Ph,Me}Zn{-}OCOOMe}$ in an open vessel with methyl iodide in $CDCl_3$ produced $\mathrm{Tp^{Ph,Me}Zn{-}I}$, methanol, and a small amount of dimethyl ether. This reaction explains why our previous attempts to convert zinc−alkyl carbonate complexes into dialkyl carbonates with methyl iodide[36,37] were unsuccessful. The nucleophilicity of **3** is so high that its reaction with methyl iodide withdraws it from equilibrium mixtures, even if it exists only in minute concentrations.

Dehydrogenations. A second basic property of mononuclear zinc alkoxides, due to their electron rich nature, should be the labilization of the alkoxide's α-CH function toward removal of the H atom as a hydride. While the simplest consequence of this, the thermolytic conversion to a zinc hydride and an aldehyde in terms of a β-elimination, has not been observed for zinc alkoxides yet, it is a common property of organometallic alkoxide complexes of the late transition metals.[38,39] In zinc chemistry it is the basis of the proposed mechanism of action of the enzyme alcoholdehydrogenase.[30] In an attempt to model this we had previously tried to oxidize the isopropoxide **8** (which was prepared in situ and not isolated) with a NAD^+ analogue to acetone.[4] Yet the reactions were not clean and the detected amount of acetone was quite small.

We therefore now resorted to a simpler variation of the theme, the use of the isopropoxide **5** for the Meerwein−Ponndorf−Verley reaction, i.e., the hydrogen transfer between an electron-rich alcohol and an electron-poor aldehyde that is normally catalyzed by Al^{3+} under basic conditions.[40] This approach had been used by other groups before, who confined themselves to the spectroscopic detection of the reaction products.[23,41] We could now show that reaction 3 occurs readily and isolate the resulting benzyl oxide complexes in good yields.

$$\underset{\mathbf{5}}{\mathrm{Tp^{Ph,Me}Zn{-}OCHMe_2}} + \underset{\mathbf{a{-}c}}{\mathrm{ArCHO}} \rightarrow \underset{\mathbf{9a{-}c}}{\mathrm{Tp^{Ph,Me}Zn{-}OCH_2Ar}} + \mathrm{(CH_3)_2CO} \qquad (3)$$

$$\mathbf{a},\ \mathrm{Ar} = \mathrm{C_6H_5};\ \mathbf{b},\ \mathrm{Ar} = \mathrm{C_6H_4}\text{-}o\text{-}\mathrm{NO_2};\ \mathbf{c},\ \mathrm{Ar} = \mathrm{C_6H_4}\text{-}p\text{-}\mathrm{NO_2}$$

Equimolar amounts of the reagents were heated in toluene. The reaction with benzaldehyde required refluxing, and the nitrobenzaldehydes reacted at 50 °C. Quantitative consumption of **5** was witnessed by ^1H NMR, as was the formation of acetone. The benzyl oxides **9** were isolated in 60−70% yield. Thus, while the direct hydride transfer from **5** to an external oxidant could not be achieved, the implicit one according to reaction 3 has proved the expected labilization of the zinc alkoxides' α-CH function.

Heterocumulene Insertions. During our attempts[6−8] to model carbonic anhydrase,[42] we had previously studied the insertions of heterocumulenes into the Zn−OH bond of Tp*Zn−OH complexes.[7] Assuming that the Tp*Zn−OR complexes are equally prone to insertion reactions as the Tp*Zn−OH complexes, one could envisage that in their case the primary insertion products could be isolated and that their structures would model the structures of the analogous insertion products resulting from Tp*Zn−OH. In the case of CO_2 insertion, there exists a firm basis for this assumption in the well-investigated reactions of metal alkoxides with CO_2 producing metal alkyl carbonates,[15] as well as in our observations that Tp*Zn−OH complexes in alcoholic solutions, which contain traces of the equilibrium species Tp*Zn−OR (see above), react with CO_2 to form the alkyl carbonate complexes Tp*Zn−OCOOR.[8,36] It remained to be verified that the alkoxides Tp*Zn−OR are really the species reacting with CO_2, and it had to be tested whether other heterocumulenes undergo analogous insertion reactions.

On the basis of the assumption that the isolated complexes are the primary insertion products, their structures should also yield mechanistic information. The accepted mechanism for the CO_2 insertion into a Zn−OH function involves a four-center intermediate in which the OH oxygen is attached to the CO_2 carbon and one CO_2 oxygen is attached to zinc.[43,44] This intermediate yields the zinc−bicarbonate complex by cleavage of the Zn−OH bond. Applied to other heterocumulenes and Zn−OR functions, this means that in the insertion products the most basic heteroatom will be bound to zinc and the OR group will be bound to the heterocumulene carbon.

The work presented in this paper was undertaken to test the above-mentioned ideas by using CO_2, CS_2, isothiocyanates, and isocyanates as heterocumulenes, which were to be reacted with the alkoxides $\mathrm{Tp^{Ph,Me}Zn{-}OR}$ for $R = CH_3$ and C_2H_5 (**3** and **4**).

Carbon Dioxide. The expected product of CO_2 insertion into a zinc alkoxide function is a zinc−alkyl carbonate. We

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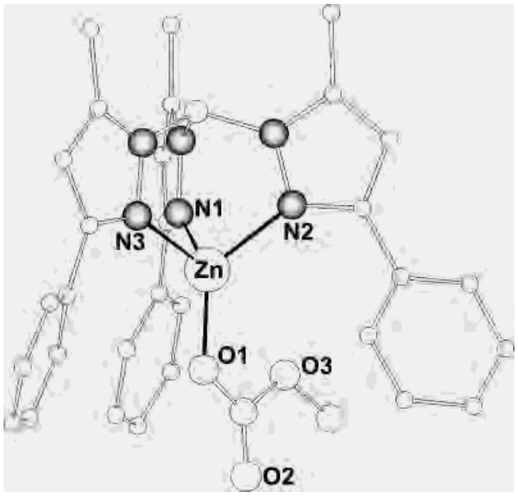

Figure 2. Molecular structure of $Tp^{Ph,Me}Zn-OC(O)OMe$ (**10**).

had already prepared various Tp*Zn−alkyl carbonates before, either by cleavage of dialkyl pyrocarbonates with Tp*Zn−OH[6] or by treatment of alcoholic solutions of Tp*Zn−OH with CO_2.[8,36] Hence in the present study only the simplest of the alkoxide complexes, **3**, was subjected to a CO_2 reaction in order to verify that the Zn−OR function is undergoing the insertion process.

The reaction, performed in carefully dehydrated solvents, took place and produced the expected complex $Tp^{Ph,Me}Zn-OC(O)OMe$ (**10**). Yet, like the other CO_2 reactions in the Tp*Zn system,[8,36] it was slow, requiring prolonged bubbling of CO_2 through the solution or applying CO_2 pressure in an autoclave. The reaction is actually slower than the one with $Tp^{Ph,Me}Zn-OH$ in methanol leading to the same product **10**. At present we can offer no convincing explanation for this puzzling observation, which we have also made for several hydrolytic cleavages with Tp*Zn−OH, which seem to be catalyzed by methanol.[45] Spectroscopy of the reaction solutions showed no other product than **10**, the methyl carbonate ligand of which is characterized by an IR band at 1714 cm^{-1}, a ^1H NMR resonance for the OMe group at 2.44 ppm, and ^{13}C NMR resonances at 52.7 ppm for OMe and at 157.8 ppm for the carbonate carbon atom.

The molecular structure of **10** is shown in Figure 2. The coordination of zinc corresponds to that in the other Tp*Zn−alkyl carbonate complexes,[6,8] including the typical Zn−O distance of 1.89 Å. As observed before,[7] there is a slight tendency of the zinc ion in such complexes to become trigonal bipyramidal by interaction with one of the carbonate donor atoms, in this case O3. This is not so much expressed in the Zn−O3 distance (2.77 Å) but in the N3−Zn−O3 angle (164°) and in the bending away of O1, narrowing the N3−Zn−O1 angle (112°) in comparison to N1−Zn−O1 (128°) and N2−Zn−O1 (126°).

Carbon Disulfide. We had already observed the facile insertion of carbon disulfide into the Zn−H and Zn−OH functions.[7] Now we found that the insertion into the Zn−OR function is equally facile. The simple alkoxides **3** and **4** reacted instantly with CS_2 according to ^1H NMR, producing high isolated yields of the xanthogenate complexes **11a** and **11b**

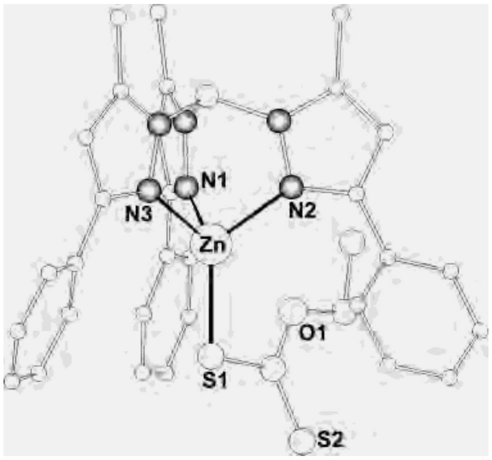

Figure 3. Molecular structure of $Tp^{Ph,Me}Zn-SC(S)OEt$ (**11b**).

$$Tp^{Ph,Me}Zn-SC(S)OR$$
11a, $R = CH_3$; **11b**, $R = C_2H_5$

(of which **11a** had been obtained before[7] from the CS_2 reaction of $Tp^{Ph,Me}Zn-OH$ in methanol). The trifluoroethoxide $Tp^{Ph,Me}Zn-OCH_2CF_3$ reacted considerably slower and only sluggishly forming $Tp^{Ph,Me}Zn-SC(S)OCH_2CF_3$, and according to ^1H NMR, there was no reaction between CS_2 and the hexafluoroisopropoxide $Tp^{Ph,Me}Zn-OCH(CF_3)_2$. These observations indicate that the nucleophilicity of both reagents is influential, the simple alkoxides being more nucleophilic than the fluoroalkoxides and the sulfur atoms of carbon disulfide being more nucleophilic than the oxygen atoms of carbon dioxide.

The spectra of complexes **11** are in accord with their structures. The most characteristic feature (difficult to observe due to relaxation problems) is the ^{13}C NMR resonance of the xanthogenate carbon, which occurs at 221.7 ppm for **11a**. The structure of **11a** has already been reported,[7] and the one of **11b** is displayed in Figure 3. The Zn−S bond length in **11b** (2.26 Å) corresponds to expectation.[7,8] There is a general similarity of the structures of complexes **10** and **11**. The major difference lies in the bond angles at the zinc-bound heteroatoms: Zn−O−C in **10**, 121°; Zn−S−C in **11a**, 98°, and in **11b**, 96°. Again a slight tendency for a trigonal bipyramidal coordination of zinc is noticeable from the Zn−O1 distance of 2.69 Å in **11a** and 2.63 Å in **11b** and from the N3−Zn−O1 angles of 173° in **11a** and 179° in **11b**.

Isothiocyanates. Previously, we made one accidental observation indicating that isothiocyanates may be inserted into Zn−OR bonds: the reaction of $Tp^{Ph,Me}Zn-OH$ with *p*-nitrophenyl isothiocyanate in chloroform containing traces of ethanol yielded complex **13b**, which was characterized by a structure determination.[7] We now verified this with complexes **3** and **4**. Their reactions with isothiocyanates were found to be considerably slower than with CS_2, and they require some activation on the side of the isothiocyanates. The least electrophilic one, methyl isothiocyanate, did not

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[45] Brombacher, H.; Peter, A.; Gross, F.; Vahrenkamp, H. Unpublished results.

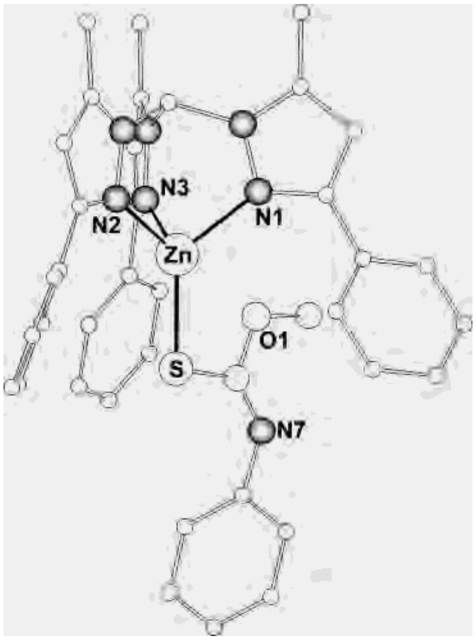

Figure 4. Molecular structure of $\mathrm{Tp^{Ph,Me}Zn{-}SC(NPh)OMe}$ (**12a**).

react. Phenyl isothiocyanate required heating to 50 °C for the reactions to proceed to the formation of **12a** and **12b**,

$$\mathrm{Tp^{Ph,Me}Zn{-}SC(NPh)OR}$$

12a, $R = CH_3$; **12b**, $R = C_2H_5$

and it did not react with $\mathrm{Tp^{Ph,Me}Zn{-}OCH_2CF_3}$. *p*-Nitrophenyl isothiocyanate reacted with both alkoxides, and the new reaction producing **13a** is reported here.

$$\mathrm{Tp^{Ph,Me}Zn{-}SC(NC_6H_4\text{-}\mathit{p}\text{-}NO_2)OR}$$

13a, $R = CH_3$; **13b**, $R = C_2H_5$

The iminothiocarbonate complexes **12** and **13** are characterized by ν(CN) IR bands above 1600 cm^{-1}. Their alkoxide ^{1}H NMR resonances are shifted upfield by 0.6−0.8 ppm in comparison to those of the starting complexes **3** and **4**, due to the embedding of the OR groups between two phenyl rings of the $\mathrm{Tp^{Ph,Me}}$ ligands. This feature is evident from the molecular structures of **13b**[7] and **12a** (Figure 4). The crystal structure of **12a** is unusual insofar as the asymmetrical unit of the triclinic unit cell contains two nearly superimposable complex molecules that nevertheless are not related to one another by crystallographic symmetry. The molecular features of **12a** are as expected. The Zn−S bond length (2.27 Å) corresponds to those in **13b**,[7] **11a**,[7] and **11b** (see above). The interaction between zinc and the OR oxygen in **12a** (2.55 Å) is stronger than in **13b** (2.68 Å),[7] again in accord with a N2−Zn−O1 angle of 176°. This in turn is in agreement with the structures of iminothiocarbonate complexes of rhenium[46] and copper[47] in which the carbonic acid derived ligands are truely bidentate.

Isocyanates. Previously we had not been able to subject isocyanates to insertion reactions with Tp*Zn−X complexes. The high nucleophilicity of the Tp*Zn−alkoxides made this possible now. Yet only the most reactive isocyanate, *p*-nitrophenyl isocyanate, and only the simplest alkoxide, **3**, underwent a clean reaction producing the insertion product **14**.

$$\mathrm{Tp^{Ph,Me}Zn{-}N(C_6H_4\text{-}\mathit{p}\text{-}NO_2){-}CO{-}OMe}$$

14

As crystals of **14** suitable for a structure determination could not be obtained, its structural assignment rests only on its spectra. The major piece of evidence is the ν(CO) IR band at 1692 cm^{-1}, which is typical for N-bound metal carbamate complexes[48,49] and which rules out the alternative Zn−O−C(NR)−OMe configuration. The ^{1}H NMR resonance of the OMe group at 2.40 ppm in $CDCl_3$ is shifted upfield by 0.63 ppm relative to that of the starting complex **3**. As discussed above for the iminothiocarbonate complexes **12** and **13**, this relates to the position of the OMe group between two phenyl rings of the $\mathrm{Tp^{Ph,Me}}$ ligand. Thus, the insertion of the isocyanate has completed the series of heterocumulene insertions, and the structure of the insertion product **14** conforms to the mechanistic proposals discussed below.

Conclusions

The facile synthesis of the pyrazolylborate−zinc alkoxides **3**−**8** with inert-atmosphere techniques has made these complexes available in good quantities for extensive studies. Their characteristic NMR data facilitate the investigation of their reactions. This paper has shown that the expected basic properties of the zinc alkoxide are quite pronounced. The methylation reactions have identified the alkoxides as unusually strong nucleophiles. The hydride transfer reactions have confirmed that the high electron density on the alkoxide ligands also labilizes their α-CH functions.

The four types of insertion reactions have verified the assumptions made to explain the related reactions of Tp*Zn−OH complexes in alcoholic media.[7,8] The Tp*Zn−alkoxides are the reactive species in the Tp*Zn−OH/alcohol mixtures, despite their extremely low concentrations in these mixtures. Their reactivity is higher than that of the Tp*Zn−hydroxides, as evidenced by their alkylation reactions with methyl iodide in the presence of a large excess of Tp*Zn−OH and by the fact that unlike any previously investigated Tp*Zn−X species they react with an isocyanate.

A comparison of the reaction rates for all insertion reactions makes it evident that nucleophilicity on the side of the heterocumulenes is also essential. CS_2 reacts fastest, followed by RNCS, RNCO, and finally CO_2. This indicates that in a rate-determining step there must be an interaction between zinc and a donor atom of the heterocumulene. This donor is a sulfur atom of CS_2 and RNCS, the nitrogen of RNCO, and one oxygen of CO_2. A logical explanation for

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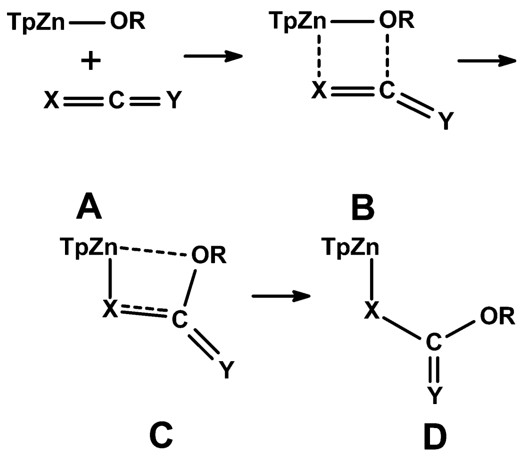
these observations is the proposal that all insertions proceed according to the four-center mechanism established for the carbonic anhydrase-catalyzed hydration of CO_2 via CO_2 insertion into the Zn−OH function.[43,44] The general formulation of the reaction course for heterocumulenes X═C═Y would then be



In each case, the most nucleophilic of the heterocumulene's donor atoms, X, which approaches the zinc ion at the beginning of the reation, remains bound to it in the isolated product, and in each case, the Zn−OR bond is broken and the leaving group, OR, remains attached to the heterocumulene's carbon atom. Thus, the reactivity sequences and the product structures give full support to the four-center mechanism, thereby fulfilling the expectations at the beginning of our work with the Tp*Zn−alkoxides.

The molecular structures of all insertion products (refs 7, 8, and this work) show one feature that can be called a witness of the four-center mechanism: one donor atom of the carbonate-derived ligand (in this work always the OR oxygen) remains weakly coordinated to the zinc ion, corresponding to stage **C** on the mechanistic pathway. For all the structure determinations this also means that all central atoms of the carbonate-derived ligand plus zinc plus the nitrogen atom trans to the weakly coordinated atom form one plane. This is the plane in which the heterocumulene approaches the zinc center, making it five-coordinate, and in which the leaving group moves away, allowing the zinc ion to become four-coordinate again, in agreement with the structure correlation analysis put forth by us to describe substrate interconversions with Tp*Zn−OH complexes.[50] This is a new contribution of pyrazolylborate−zinc chemistry to the understanding of zinc-catalyzed reactions.

Experimental Section

General Data. All experimental techniques and the standard IR and NMR equipment were as described previously.[51] All manipulations involving the Tp*Zn−alkoxide complexes were performed in a Braun Labmaster 130 glovebox with degassed and dried solvents. The complexes Tp^{Ph,Me}ZnOH[25] and Tp^{Ph,Me}Zn−H[33] were prepared as described. Organic reagents were purchased from Merck and Aldrich. The IR, ^{1}H NMR, and ^{13}C NMR spectral data for the Tp^{Ph,Me} and Tp^{Cum,Me} ligands in the new complexes vary only negligibly between themselves and the reference compounds.[3,8,25,33] Therefore, only the data for the coligands X in the Tp*Zn−X complexes are reported here. A frequent problem with the elemental analyses of this kind of complexes is that the carbon values found are too low. When this was the case here, at least one (but normally two) additional elemental analysis value (N, S, or Zn) was determined.

All preparations of starting complexes, of the zinc alkoxide complexes as well as the details of the equilibrium studies of Tp^{Ph,Me}Zn−OH in methanol are given in the Supporting Information.

Methylations. These reactions, all products of which are known compounds, were monitored by ^{1}H NMR spectroscopy. The reagents were taken from 0.08 M stock solutions in $CDCl_3$. Equimolar amounts of the zinc complex and of methyl iodide (0.5 mL each) were combined in NMR tubes.

3: The reaction was complete after 2 h. Dimethyl ether was recognized by its ^{1}H NMR resonance at 3.30 ppm.

4: The reaction was complete after 3 h. Methyl ethyl ether was recognized by its ^{1}H NMR data: 1.18 (t, $J = 7.0$ Hz, 3H, CCH_3), 3.31 (s, 3H, CH_3), 3.35 (q, $J = 7.0$ Hz, 2H, H_2).

Tp^{Ph,Me}Zn−OH: The reaction was complete after 4 d, during which time the major part of the reaction products methanol and dimethyl ether had already evaporated through the stopper of the NMR tube. After completion the OMe NMR resonances of methanol (3.42 ppm) and of dimethyl ether (3.30 ppm) showed an intensity ratio of roughly 2:1.

Tp^{Ph,Me}Zn−OCOOMe: The reaction was complete after 6 d. After this time the amounts of methanol and dimethyl ether in solution corresponded to product yields of 50 and 6%, respectively.

Meerwein−Ponndorf−Verley Reactions. With Benzaldehyde. A solution of **5** (200 mg, 0.33 mmol) and benzaldehyde (33 μL, 35 mg, 0.33 mmol) in toluene (30 mL) was refluxed for 7 h. Reducing the volume to one-half in vacuo and cooling to −20 °C precipitated 127 mg (59%) of colorless **9a**, mp 197 °C. IR(KBr): 2445w (BH). ^{1}H NMR ($CDCl_3$): 4.28 (s, OH_2).

Anal. Calcd for $C_{37}H_{35}BN_6OZn{\cdot}$toluene ($M_r = 655.9 + 92.1$): C, 70.65; H, 5.79; N, 11.23. Found: C, 69.12; H, 5.94; N, 11.18.

With *o*-Nitrobenzaldehyde. The reaction was like the above with **5** (150 mg, 0.25 mmol) and *o*-nitrobenzaldehyde (38 mg, 0.25 mmol). Yield 107 mg (62%) of colorless **9b**, mp 210 °C (dec). IR (KBr): 2550w (BH). ^{1}H NMR ($CDCl_3$): 4.17 (s, OH_2).

Anal. Calcd for $C_{37}H_{34}BN_7O_3Zn$ ($M_r = 700.9$): C, 63.40; H, 4.89; N, 13.99. Found: C, 63.20; H, 5.12; N, 14.01.

With *p*-Nitrobenzaldehyde. The reaction was like the above with **5** (150 mg, 0.25 mmol) and *p*-nitrobenzaldehyde (38 mg, 0.25 mmol). Yield 121 mg (70%) of colorless **9c**, mp 224 °C. IR (KBr): 2541w (BH). ^{1}H NMR ($CDCl_3$): 4.20 (s, OH_2).

Anal. Calcd for $C_{37}H_{34}BN_7O_3Zn$ ($M_r = 700.9$): C, 63.40; H, 4.89; N, 13.99. Found: C, 63.26; H, 5.15; N, 14.07.

CO_2 Reaction with 3. To ensure the absence of methanol or water in the reaction mixture, both the solvents and the CO_2 were subjected to two dehydrating cycles. Carbon dioxide was bubbled at room temperature through a solution of 200 mg (0.34 mmol) of **3** in 20 mL of benzene and 20 mL of dichloromethane. After 6 h the colorless suspension was filtered and the filtrate brought to dryness by bubbling CO_2 through it. Then 177 mg (82%) of **10** remained as colorless crystals, mp 252 °C. IR (KBr): 2557m (BH), 1714s (CO). ^{1}H NMR ($CDCl_3$): 2.44 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$): 52.7 (OMe), 157.8 (carbonate-C). Anal. Calcd for

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Table 1. Crystallographic Data

	3	**10**	**11b**	**12a**
formula	$C_{31}H_{31}BN_6OZn$	$C_{32}H_{31}BN_6O_3Zn$	$C_{33}H_{33}BN_6OS_2Zn$	$C_{38}H_{36}BN_7OSZn$
MW	579.8	632.8	670.0	715.0
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	2	4	4	4
a (Å)	9.061(2)	11.483(1)	9.526(2)	11.388(1)
b (Å)	9.912(2)	9.875(1)	18.106(5)	17.004(1)
c (Å)	16.412(3)	27.280(2)	18.990(5)	19.105(1)
α (deg)	106.140(4)	90	90	97.976(1)
β (deg)	102.985(4)	95.902(2)	94.959(5)	90.062(1)
γ (deg)	90.631(4)	90	90	100.237(1)
V (Å^3)	1375.4(5)	3077.0(4)	3263(1)	3604.1(4)
d_{calc} (g cm^{-3})	1.40	1.35	1.36	1.32
μ(Mo Kα) (mm^{-1})	0.93	0.84	0.92	0.78
R1 (obs refl)[a]	0.051	0.040	0.066	0.048
wR2 (all refl)[a]	0.142	0.117	0.236	0.146

[a] The *R* values are defined as $R1 = \sum|F_o - F_c|/\sum F_o$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]]^{1/2}$.

$C_{32}H_{31}BN_6O_3Zn$ (M_r = 623.84): C, 61.61; H, 5.01; N, 13.47. Found C, 61.26; H, 4.95; N, 13.01.

CS_2 Reactions. With 3. 3 (200 mg, 0.35 mmol) and 208 μL (263 mg, 3.45 mmol) of CS_2 in 20 mL of toluene were stirred for 30 min. All volatiles were removed in vacuo. Recrystallization from hot acetonitrile yielded 210 mg (93%) of **11a** as colorless crystals, mp 222 °C. IR (KBr): 2551m (BH). ^{1}H NMR ($CDCl_3$): 2.64 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$): 59.0 (OMe), 221.7 (CS). Anal. Calcd for $C_{32}H_{31}BN_6OS_2Zn$ (M_r = 655.97): C, 58.59; H, 4.76; N, 12.81; S 9.78. Found: C, 58.67; H, 4.84; N, 12.81; S, 9.98.

With 4. 4 (150 mg, 0.25 mmol) and 153 μL (192 mg, 2.53 mmol) of CS_2 in 15 mL of dichloromethane were stirred for 30 min. All volatiles were removed in vacuo. Recrystallization from ethanol/dichloromethane (1:1) yielded 137 mg (91%) of **11b** as colorless crystals, mp 164 °C. IR (KBr): 2551m (BH). ^{1}H NMR ($CDCl_3$): 0.39 (t, J = 6.6 Hz, 3H, CH_3(OEt)), 2.98 (q, J = 6.6 Hz, 2H, H_2(OEt)). Anal. Calcd for $C_{33}H_{33}BN_6OS_2Zn$ (M_r = 670.00): C, 59.16; H, 4.96; N, 12.54; S, 9.57. Found: C, 59.06; H, 5.09; N, 12.46; S, 9.37.

Isothiocyanate Reactions. 3 and PhNCS. 3 (200 mg, 0.35 mmol) and 42 μL (47 mg, 0.35 mmol) of PhNCS in 15 mL of toluene were stirred at 50 °C for 1 d. The volume of the solution was reduced to one-half in vacuo and the solution was kept at −20 °C, precipitating 180 mg (73%) of **12a** as colorless crystals, mp 244 °C. IR (KBr): 2549m (BH), 1630s (CN). ^{1}H NMR ($CDCl_3$): 2.32 (S, 3H, OMe). Anal. Calcd for $C_{38}H_{36}BN_7OSZn$ (M_r = 715.02): C, 63.83; H, 5.07; N, 13.71; S, 4.48. Found: C, 63.30; H, 5.14; N, 13.66; S, 4.57.

4 and PhNCS. The reaction was like the above with 150 mg (0.25 mmol) of **4** and 30 μL (34 mg, 0.25 mmol) of PhNCS. Yield 109 mg (59%) of **12b** as a colorless powder, mp 232 °C. IR (KBr): 2549m (BH), 1629s (CN). ^{1}H NMR ($CDCl_3$): 0.13 (t, J = 7.2 Hz, 3H, CH_3(OEt)), 2.71 (q, J = 7.2 Hz, 2H, H_2 (OEt)). Anal. Calcd for $C_{39}H_{38}BN_7OSZn$ (M_r = 729.04): C, 64.25; H, 5.25; N, 13.45; S, 4.40. Found: C, 64.23; H, 5.46; N, 13.60; S, 4.48.

3 and *p*-Nitrophenyl-NCS. A mixture of 200 mg (0.35 mmol) of **3** in 10 mL of dichloromethane and 62 mg (0.35 mmol) of *p*-nitrophenyl-NCS in 10 mL of acetonitrile was stirred for 24 h. All volatiles were removed in vacuo. Recrystallization from hot acetonitrile yielded 204 mg (78%) of **13a** as yellow crystals, mp 230°C. IR (KBr): 2539m (BH), 1614s (CN). ^{1}H NMR ($CDCl_3$): 2.37 (s, 3H, OMe). Anal. Calcd for $C_{38}H_{35}BN_8O_3SZn$ (M_r = 760.01): C, 60.05; H, 4.64; N, 14.74; S, 4.22. Found: C, 59.97; H, 4.72; N, 14.78; S, 4.20.

Isocyanate Reaction of 3. 3 (200 mg, 0.35 mmol) and 57 mg (0.35 mmol) of *p*-nitrophenyl-NCO in 20 mL of toluene were refluxed for 15 h. The solvent was removed in vacuo, and the residue picked up in 10 mL of hot acetonitrile and then kept at −20 °C, precipitating 98 mg (41%) of **14** as an orange powder, mp 255 °C (dec). IR (KBr): 2545m (BH), 1692s (CO). ^{1}H NMR ($CDCl_3$): 2.40 (s, 3H, OMe). Anal. Calcd for $C_{38}H_{35}BN_8O_4Zn$ (M_r = 743.95): C, 61.35; H, 4.74; N, 15.06. Found: C, 61.27; H, 4.81; N, 15.23.

Structure Determinations. Crystals of **3** were obtained by diffusion of CH_2Cl_2 into a methanol solution. Crystals of **10**, **11b**, and **12a** were obtained from the reaction solutions. Diffraction data were obtained at room temperature with a Bruker Smart CCD diffratometer and subjected to empirical absorption corrections. The structures were solved with SHELX.[52] Parameters were refined against F^2. Drawings were produced with SCHAKAL.[53] Table 1 lists the crystallographic data.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We are indebted to Prof. C. Röhr and Drs. W. Deck and M. Rombach for assistance, Mrs. P. Klose for help with the preparations, and Drs. C. Sudbrake and R. Walz for providing samples of starting materials.

Supporting Information Available: Preparations of starting materials and of all Tp*Zn−OR complexes. Details of the equilibration measurements on $Tp^{Ph,Me}Zn-OH$ in methanol. Fully labeled ORTEP plots and X-ray crystallographic files in CIF format for the four structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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