Sulfur-Rich Zinc Chemistry: New Tris(thioimidazolyl)hydroborate Ligands and Their Zinc Complex Chemistry Related to the Structure and Function of Alcohol Dehydrogenase

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Received January 30, 2001

The 1-substituted tris(2-thioimidazolyl)hydroborate ligands Tt^R were prepared as the potassium salts from KBH_4 and the corresponding 1-R-2-thioimidazole for R = *t*-Bu and C_6H_4-*p*-$CH(CH_3)_2$ (Cum). Their reactions with zinc salts yielded the tetrahedral complexes Tt^RZn-X with X = F, Cl, ONO_2 and $(Tt^{t\text{-}Bu})_2Zn$. With zinc perchlorate the labile perchlorate complexes $Tt^RZn-OClO_3$ were obtained. They served as starting materials for the incorporation of substrates which are relevant for the chemistry of horse liver alcohol dehydrogenase: Ethanol led to $[Tt^{t\text{-}Bu}Zn\cdot EtOH]\ ClO_4\cdot EtOH$, *p*-nitrophenol (NitOH) yielded $Tt^{Cum}Zn-ONit$. Pyridine-2-carbaldehyde and salicylic aldehyde were incorporated as N(pyridine) and O(phenolate) coligands with possible additional O(aldehyde) coordination. Substituted pyridyl methanols ($R-PyCH_2OH$) yielded the trinuclear complexes $[(Tt^{t\text{-}Bu})_2Zn_3(R-PyCH_2O)_2]\ (ClO_4)_2$ with bridging Tt and pyridylmethoxide ligands. Preliminary experiments on the functional modeling of alcohol dehydrogenase have shown that TtZn complexes promote both the dehydrogenation of 2-propanol and the hydrogenation of pentafluorobenzaldehyde.

Introduction

Sulfur-rich environments of zinc, typically with a tetrahedral coordination, are common in the mineral world (zinc blende, wurtzite) as well as in living matter (structural zinc in enzymes, zinc fingers, etc.). But while ZnS_4, $ZnNS_3$, and ZnN_2S_2 (N and S representing histidine and cysteinate) coordinations are the preferred ones for structural zinc, they are quite unusual for catalytic zinc which is predominantly linked to the protein environment by N(histidine) and O(glutamate, aspartate).[1,2] In this respect the enzymes horse liver alcohol dehydrogenase,[3] cytidine deaminase,[4] and spinach carbonic anhydrase,[5] which bind zinc in the active center by a NS_2 (histidine, cysteinate, cysteinate) ligation, are unusual. Their zinc centers are very soft and uncharged due to the attachment of the two anionic cysteine residues and hence cannot be the typical Lewis acid centers which normally exert the catalytic functions of zinc in biology. On the other hand this may be the basis for the unusual binding abilities of zinc toward alcohols, alkoxides and aldehydes during the catalytic turnover of alcohol dehydrogenase.[6]

Both the uncharged nature and the bis(thiolato)zinc coordination of the (N,S,S)Zn−X centers have proven themselves as unfinished challenges in zinc model complex chemistry until today. The high tendency of zinc-bound thiolate units to become bridging units in oligonuclear complexes[7] has rendered futile all attempts to employ amine-bis(thiolate) ligands for the synthesis of mononuclear tetrahedral (N,S,S)Zn−X complexes.[8−12] Likewise, some very attractive tripodal tris-thiol ligands[13] were found to be useless for the synthesis of mononuclear zinc complexes. The main reason the model complex chemistry fails in this respect is the bonding nature of the thiolate sulfur itself: its divalent character does not allow the attachment of additional substituents at sulfur which would provide the steric hindrance which is self-evident in the active center of an enzyme.

It therefore seems inevitable to modify the electronic nature of the sulfur donors in model ligands. That this may be sucessful has recently been shown by Riordan[14] and Berreau[15] for (N,S,S)-Zn−X complexes derived from tripodal thioether ligands. Yet thioethers are too distant relatives of thiolates, and it would be more suitable to have "tame" thiolates, i.e., those with a reduced basicity or bridging tendency. In this respect Reglinski's thioimidazolylborate ligands[16−19] mark a breakthrough. Their thioimidazolyl sulfur donors are "hidden" thiolate donors

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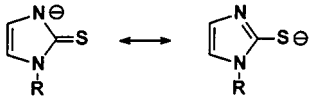
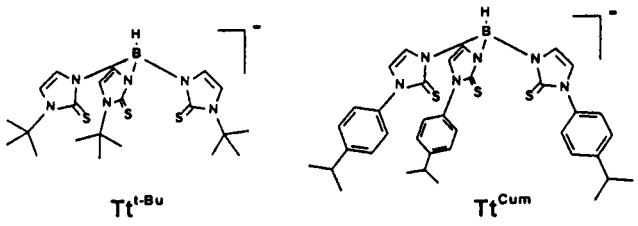
10.1021/ic0101275 CCC: $20.00
Published on Web 07/04/2001

according to the following resonance formulation which shows that they are not as basic as thiols and do not bear a full negative charge.



Following the first report on the tris(1-methyl-2-thioimidazolyl)hydroborate[16] Reglinski[16,18] and Parkin[20,21] could show that ligands of this kind are indeed suitable for a biomimetic zinc complex chemistry. In addition Parkin demonstrated that the mixed bis(thioimidazolyl)(pyrazolyl)hydroborates open the way to tetrahedral (N,S,S)Zn−X complexes.[21,22] It became obvious too, however, that such complexes have a tendency for dismutation, resulting in neutral bis(ligand) complexes with a ZnS_4 coordination.[23]

Our own work in this field was also triggered by Reglinski's first communication,[16] and we too ran into the problem of redistribution and bis(ligand) complex formation. We therefore resorted to the approach which was so sucessful for us in pyrazolylborate zinc complex chemistry, the encapsulation of the metal by large substituents on the three ligand arms.[24] This paper reports some of our results in the zinc chemistry of tris(thioimidazolyl)hydroborates, aiming at basic information for the modeling of alcohol dehydrogenase. Our work complements and extends the work by Parkin[20] with similar sterically hindered thioimidazolylborates. Parallel to this work we have also prepared bis(thioimidazolyl)(pyrazolyl)hydroborate ligands with similar substitution patterns which have allowed the synthesis of the first correct structural model of alcohol dehydrogenase in the form of a (N,S,S)Zn−ethanol complex.[25]



For the nomenclature of ligands and complexes we adopt a scheme derived from that of the tris(pyrazolyl)hydroborate ligands ($Tp^{R,R}$, with R and R′ naming the substituents at the 3- and 5-positions of the pyrazole rings). We call the tris(2-thioimidazolyl)hydroborate ligands Tt^R, with R naming the substituents at the 1-positions of the imidazole rings. Thus the two ligands used in this study are $Tt^{t\text{-}Bu}$ and Tt^{Cum}.

Results and Discussion

Ligands. The synthesis of the Tt ligands is completely analogous to that of the Tp ligands, i.e., they result as potassium salts from a thermal reaction between KBH_4 and the corresponding thioimidazole. It turned out, however, that $KTt^{t\text{-}Bu}$ and KTt^{Cum} could be obtained under much milder conditions than similar KTp compounds. Both were prepared in good yields in boiling toluene from which they were isolated analytically pure by precipitation. Their only typical feature in the IR is a low-intensity ν(BH) band above 2500 cm^{-1}. In the NMR they show a characteristic pair of doublets in the 6−7 ppm range for the two imidazole protons.

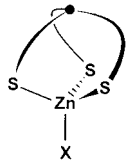


Figure 1. Schematic drawing of the ligand arrangement in TtZn−X complexes.

Simple Complexes. The potassium salt of $Tt^{t\text{-}Bu}$ was used to explore the basic zinc complex chemistry of these ligands. Its reaction with zinc chloride and zinc nitrate allowed the straightforward synthesis of **1** and **3**. Metathetical reaction between **3** and potassium fluoride yielded **2**. Complexes **1**−**3** express a typical feature of the other complexes of this study, insofar as they combine the very soft TtZn unit with harder (typically oxygen-containing) coligands. In contrast, a TtZn-thiolate complex has eluded us so far.

$Tt^{t\text{-}Bu}ZnCl$ **1** $Tt^{t\text{-}Bu}Zn\text{-}F$ **2** $Tt^{t\text{-}Bu}Zn\text{-}ONO_2$ **3**

Complexes **1**−**3** define the basic structural features of all our TtZn complexes. Figure 1 symbolizes the main structural characteristic: unlike for the TpZn complexes where the planes of the three pyrazole rings are paralel to and include the molecular 3-fold axis, for the TtZn complexes the planes of the three imidazole rings are tilted by 50−60° with respect to the B−Zn axis (which in the case of $Tt^{t\text{-}Bu}Zn-F$ is a crystallographic 3-fold axis) in the same direction, thereby defining a propeller-like arrangement. The reason for this is the conflict between the conformational requirements of the eight-membered chelate rings and the tetrahedral nature of zinc. The resulting arrangement seems to be strain-free: in all six TtZn−X structures described here the S−Zn−S angles (105−110°) are close to the tetrahedral value and the Zn−S distances are all in the very narrow range of 2.32−2.35 Å. As a result, however, the *tert*-butyl substituents are not really encapsulating the zinc ion, but rather point away from it. Thus in complexes **1**−**3** the cone angle at zinc is about 155°, almost twice as large as that in $Tp^{t\text{-}Bu}$ zinc complexes. This in turn means that it is considerably more cumbersome to construct a sterically confined environment for the zinc ion in TtZn complexes.

The other details of the molecular structures of **1**−**3** are not unusual. Figure 2 shows the molecules of **1** and **2**. Figure 3 focuses on the semibidentate nature of the nitrate ligand which is quite similar to that in $Tp^{t\text{-}Bu}Zn-ONO_2$.[26]

Another simple complex of the undesirable 2:1 composition was obtained by adding zinc perchlorate to a solution of $KTt^{t\text{-}Bu}$ and extracting with nonpolar solvents. The molecular nature of the product **4** was obvious from its solubility, and it was confirmed by the structure determination (Figure 4). **4** extends the list of such ZnS_4 species derived from thioimidazolylborate ligands.[21,23,24,27] Its Zn−S bond lengths ranging

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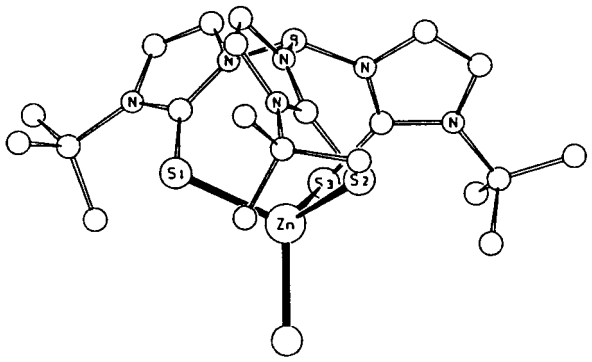

Figure 2. Molecular structures of **1** (Zn−Cl, 2.239(1) Å) and **2** (Zn−F, 1.85(1) Å).

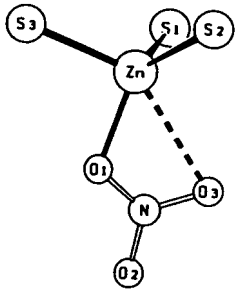

Figure 3. Zinc coordination in $Tt^{t\text{-}Bu}Zn{-}ONO_2$ (**3**, major component of a 7:3 composition of disordered nitrate ligands). Zn−O1, 2.014(4); Zn−O3, 2.719(5) Å.

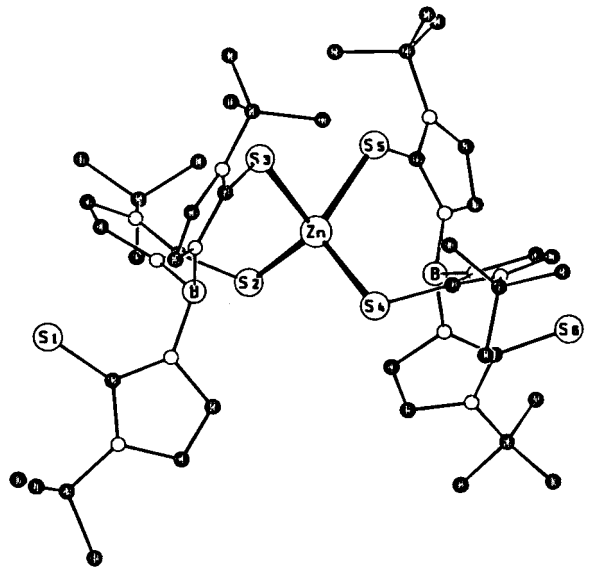

Figure 4. Molecular structure of $(Tt^{t\text{-}Bu})_2Zn$ (**4**). Zn−S2, 2.372(1); Zn−S3, 2.413(1); Zn−S4, 2.356(1); Zn−S5, 2.384(1) Å. S2−Zn−S3, 111.53(3)°; S2−Zn−S4, 109.11(3)°; S2−Zn−S5, 118.58(3)°; S3−Zn−S4, 115.33(3)°; S3−Zn−S5, 85.58(3)°; S4−Zn−S5, 115.15(3)°.

from 2.36 to 2.41 Å and its very wide spread of S−Zn−S angles resemble those in the known complexes.

$(Tt^{t\text{-}Bu})_2Zn$
4

Functional Complexes. The essential species of this paper, which can be called a naked TtZn complex, was obtained by performing the $KTt^{t\text{-}Bu}/Zn(ClO_4)_2$ reaction such that there was always a large excess of $Zn(ClO_4)_2$ in solution. From this resulted, after removal of the solvent, the perchlorate complex

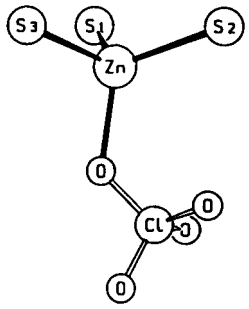

Figure 5. Zinc coordination in $Tt^{t\text{-}Bu}Zn{-}OClO_3$ (**5**). Zn−O, 2.040(3) Å. S1−Zn−O, 112.1(1)°; S2−Zn−O, 115.3(1)°; S3−Zn−O, 101.5(1)°.

5 which was crystallized solvent-free and identified by a structure determination (Figure 5).

$Tt^{t\text{-}Bu}Zn\text{-}OClO_3$
5

The Tt ligand in **5** is arranged as discussed above, and hence only the environment of the zinc ion is displayed in Figure 5. The ZnS_3O coordination is close to ideally tetrahedral. The Zn−O bond is of the same length as that in the only other tetrahedral zinc-perchlorate complex, a tris(pyrazole)-perchlorato zinc cation.[28] It is somewhat longer than the comparable bonds Zn−F in **2** and Zn−O in **3** and **6**, corresponding to the lower donor qualities of the perchlorate ligand.

It is likely that in alcoholic solution the TtZn perchlorate complex is in equilibrium with a solvated species comprised of a TtZn−alcohol cation and uncoordinated perchlorate. While from methanolic solution complex **5** was most easily isolated, crystallizations from ethanolic solution yielded the ethanol complex **6**. Complex **6** is an analogue of Parkin's $Tt^{Mes}Zn\cdot$MeOH complex.[20] The ease of formation of these TtZn·alcohol complexes is a strong indicator for the correctness of the assumption that the soft environment of zinc in alcohol dehydrogenase is a prerequisite for the attachment and interconversion of alcohols.

$[Tt^{t\text{-}Bu}Zn\cdot EtOH]\,ClO_4\cdot EtOH$
6

Complex **6** is also accessible by dissolving **5** in ethanol and precipitating with petroleum ether, a procedure which does not work when trying to prepare the corresponding methanol complex. This points to an order of binding strenghts toward the $Tt^{t\text{-}Bu}Zn$ moiety as methanol < perchlorate < ethanol. In terms of a derivative chemistry this meant that it was most favorable to use the isolated perchlorate complex or a freshly prepared methanolic solution of it for the introduction of other ligands.

The structure determination of **6** showed that the $Tt^{t\text{-}Bu}$ ligand is arranged as observed above. Therefore Figure 6 again shows the essential molecular features only. The ethanol ligand is bound to zinc with a Zn−O distance of 2.01 Å, i.e., with a comparable strength as the nitrate in **3**, somewhat stronger than the perchlorate in **5**, and noticeably weaker than the *p*-nitrophenolate in **7** (see below). Parkin's $Tt^{Mes}Zn\cdot$methanol complex has the same Zn−O distance,[20] which is also identical to the one in the pentafluorobenzyl alcohol adduct of alcohol dehydrogenase.[3] Altogether there seems to be little variation of Zn−O bond lengths in zinc−alcohol complexes, as we have

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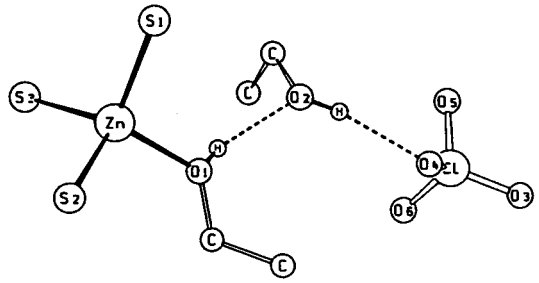


Figure 6. Zinc coordination in [Tt$^{t\text{-Bu}}$Zn·EtOH] ClO_4 (**6**, major component of a 5:1 composition of disordered ethanol ligands). Zn−O1, 2.009(3); O1···O2, 2.657(3); O2···O4, 2.833(4) Å. S1−Zn−O1, 108.9(1); S2−Zn−O1, 105.4(1)°; S3−Zn−O1, 113.0(1)°; O1−H···O2, 146.5(5)°; O2−H···O4, 169.3(5)°.

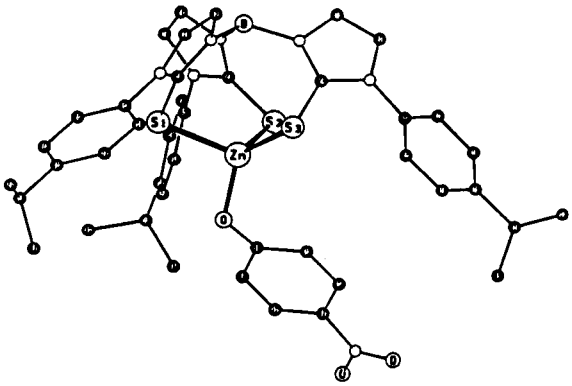


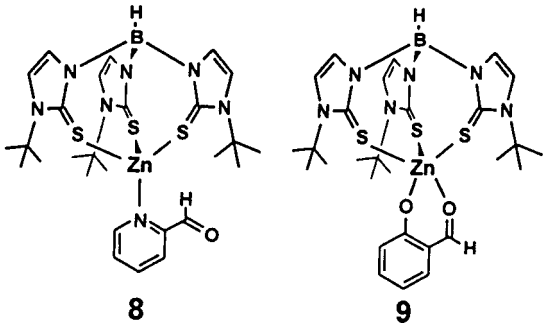
Figure 7. Molecular structure of Tt^{Cum}Zn-*p*-nitrophenolate (**7**). Zn−O1, 1.909(5) Å. S1−Zn−S2, 111.22(6)°; S1−Zn−S3, 107.00(6)°; S2−Zn−S3, 103.06(6)°; S1−Zn−O1, 104.1(2)°; S2−Zn−O1, 106.1(2)°; S3−Zn−O1, 125.3(2)°.

observed before.[29,30] The alcohol coordination in **6** is completed by the attachment of a second ethanol molecule via a hydrogen bond. The latter in turn is connected to the perchlorate anion by another hydrogen bond. Thus complex **6** reproduces the essential features of the enzymatic situation,[1−3] i.e., the alcohol coordination to a soft and tetrahedral zinc center and its involvement in a hydrogen bonding network.

The second biologically relevant form of alcohol incorporation in these complexes is that as an alkoxide. While an ethoxide derivative of a TtZn unit could not be obtained as yet, it was easy to incorporate a phenoxide. This, together with the oxidation of 2-propanol (see below), was the main application of Tt^{Cum}, the second Tt ligand used in this study. The incorporation of *p*-nitrophenolate in complex **7** was done using the Tt^{Cum}Zn-perchlorate species in methanol as an intermediate. Its treatment with *p*-nitrophenolate gave **7** in good yields. **7** is thermally quite stable, and the zinc−phenolate combination is not hydrolyzed by moisture.

$$\underset{\mathbf{7}}{Tt^{Cum}Zn\text{-}OC_6H_4\text{-}p\text{-}NO_2}$$

The structure determination of **7** revealed a significantly distorted tetrahedral ZnS_3O arrangement, which is most noticeable in the S3−Zn−O1 angle, cf. Figure 7. The propeller-like orientation of the imidazole rings is the same as that in the Tt$^{t\text{-Bu}}$Zn complexes, but the *p*-isopropylphenyl substituents provide a denser encapsulation of the Zn−X unit than the *tert*-butyl substituents. The Zn−O bond (1.91 Å) is the shortest



8 **9**

Figure 8. Proposed structures of [Tt$^{t\text{-Bu}}$Zn(PyCHO)] ClO_4 (**8**) and Tt$^{t\text{-Bu}}$Zn(OC_6H_4CHO) (**9**).

observed in this study, but it compares reasonably well with that in the closely related pyrazolylborate zinc complex Tp^{Cum,Me}Zn-*p*-nitrophenolate (1.86 Å).[31]

To further test the ability of the TtZn systems to model the substrate binding of alcohol dehydrogenase it was attempted to introduce alkoxides and aldehydes which bear an additional donor function.Thereby the chelate effect was expected to support the zinc−alkoxide and zinc−aldehyde coordinations, as was achieved by us previously for the coordination to Zn-$(SR)_2$ systems.[32] The substrates chosen were pyridine-2-carbaldehyde (PyCHO), salicylaldehyde (HOC_6H_4CHO), 2-hydroxymethylpyridine ($PyCH_2OH$), and 2-hydroxymethyl-6-methylpyridine ($MePyCH_2OH$).

Both PyCHO and potassium formylphenolate reacted smoothly with the perchlorate complex **5** and yielded the adducts [Tt$^{t\text{-Bu}}$Zn(PyCHO)] ClO_4 (**8**) and Tt$^{t\text{-Bu}}$(OC_6H_4CHO) (**9**) in very good yields. As crystals suitable for structure determinations could not be obtained, the constituions of **8** and **9** had to be deduced from their spectra. The pyridine coordination in **8** is evident from the typical shift of the pyridine ring vibration band[32] from 1585 to 1603 cm^{-1}. Neither the aldehyde ν(CO) band (1713 → 1715 cm^{-1}) nor the aldehyde CH ^{1}H NMR resonanance (10.08 → 10.10 ppm) show significant changes upon coordination, however, leading to the conclusion that the aldehyde function is not coordinated to zinc. In case of **9** both the aldeyhde ν(CO) band (1671 → 1659 cm^{-1}) and the aldehydic proton resonance (9.99 → 10.20 ppm) are shifted by the expected amounts in comparison to those of free formylphenolate.[33] Thus both the phenolate and the aldehyde function of salicylic aldehyde seem to be coordinated, in analogy to the situation in the complex Tp^{Cum,Me}Zn(OC_6H_4CHO).[33] The resulting structural assignments are given in Figure 8.

The reactions between the perchlorate complex **5** and the 2-hydroxymethylpyridines had an unexpected outcome. The resulting complexes **10a** and **10b** had a 2:3:2 (Tt/Zn/pyridine) composition which could only be ascertained by a structure determination. The overall loss of one Tt and one hydroxymethylpyridine ligand must be an expression of both the acid−base chemistry involved (deprotonation of the hydroxymethylpyridine) and the preferred coordination modes of the four chelating ligands present in the trinuclear complexes.

$$[(Tt^{t\text{-Bu}})_2Zn_3(L)_2](ClO_4)_2$$

10a: L = $PyCH_2O$ **10b:** L = $MePyCH_2O$

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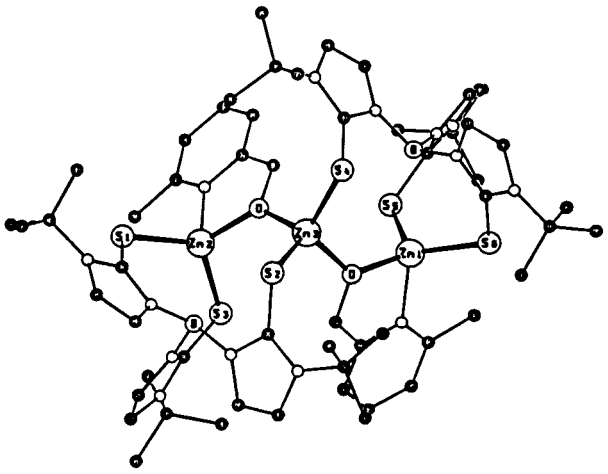


Figure 9. Structure of the $(Tt^{t-Bu})_2Zn_3(MePyCH_2O)_2$ cation of **10b**. Zn1−N14, 2.084(5); Zn2−N13, 2.067(5); Zn1−O2, 1.978(4); Zn2−O1, 1.973(4); Zn3−O2, 1.965(4); Zn3−O1, 1.966(4) Å.

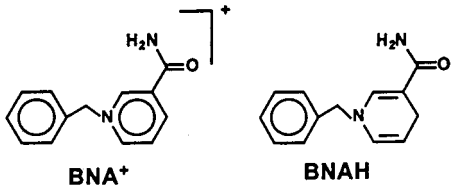
The trinuclear cations of **10b** (Figure 9) contain a bent array of the three zinc ions (Zn−Zn−Zn, 104°), each of them coordinated tetrahedrally. The two Tt ligands use two of their sulfur donors each to bind to the external zinc ions and the third each to bind to the central zinc ion. The two pyridylmethoxide ligands are coordinated with their nitrogen donors to the external zinc ions and use their alkoxide functions to bridge one external and the central zinc ion each. The resulting ZnX_4 tetrahedra are quite distorted for the external zinc ions (S−Zn−S, ca. 120°; O−Zn−N, ca. 83°) but closer to ideal for the central zinc ion (S−Zn−S, 92°; O−Zn−O, 103°). All Zn−S bond lengths are in the narrow range of 2.32−2.36 Å. The Zn−N and Zn−O bonds have the expected lengths for tetrahedral zinc, and the bridging oxygens have identical bond lengths (1.97 Å) to both their zinc ions.

Thus the chelating coligands have verified our expectations. Both the aldehyde function (in **9**) and the alkoxide function (in **10**) could be attached to zinc, albeit in an unusual way in **10**. Together with the alcoholic function in **6** and the phenoxide function in **7** they comprise the whole range of possible functions by which the oxygen-containing substrates and products of alcohol dehydrogenase can be bound to zinc. In addition, the tetrahedral $ZnNS_2O$ coordination which is present in horse liver alcohol dehydrogenase[3] is reproduced both in terms of geometry and alkoxide binding by the external $ZnNS_2O$ units in complexes **10**.

Functionality of the Complexes. Horse liver alcohol dehydrogenase catalyzes the reaction

$$CH_3CH_2OH + NAD^+ \rightarrow CH_3CHO + NADH + H^+$$

Yet the equilibrium constant of this reaction is $8\cdot10^{-12}$,[34] i.e., the oxidation requires a source of energy and only the reduction of the aldehyde is spontaneous. Because of this, model studies have focused on the reductive process and only in a few cases[35,36] has the oxidation of the electron rich alcohol 2-propanol to acetone by NAD^+ model compounds in the presence of zinc complexes been observed. The reagents of choice to model NAD^+ and NADH are the benzylnicotinamide derivatives BNA^+ (as the chloride) and BNAH.



The $Tt^{Cum}Zn$ complex **7** was used to attempt catalytic oxidations. Quantitative consumption of the oxidant (BNA)Cl was observed when reacting a mixture of **7** (0.05 mmol), (BNA)-Cl (0.05 mmol) and 2-propanol (2.6 mmol) in deuterated DMSO. Following the reaction by ^1H NMR confirmed that BNA^+ was converted to BNAH and that acetone was formed. The reaction took several hours to go to completion at 100 °C, but no acetone was formed in the absence of **7**. Thus the catalytic activity of **7** is confirmed, and it is of the same quality as obeserved for other zinc-containing catalysts before.[35,36]

The ease of the reverse reaction, the reduction of electron-poor aldehydes by BNAH, allowed a quantitative study which compares favorably with similar studies by other authors.[35,37,38] Pentafluorobenzaldehyde and pyridine-2-carbaldehyde were treated with BNAH in the presence of varying concentrations of the perchlorate complex **5** (which is the closest approximation to "naked" $Tt^{t-Bu}Zn$). The reactions were monitored by observing the intensity of the UV band of BNAH at 348 nm. Figure 10 plots the kinetic data derived from these measurements.

Figure 10 shows that the slow spontaneous decomposition of BNAH is almost uninfluenced by the presence of **5** and that in the absence of **5** the reductions of the aldehydes are insignificantly slow. The initial rates of BNAH consumption by the aldehydes are increased by increasing amounts of **5**. They level off at higher concentrations of **5** such that above ca. 1 mM of **5** no more increase is observed. The kinetic data cannot be fitted for reaction orders of 0, 1, or 2. This indicates the presence of complex equilibria involving coordination of the aldehydes (specifically pyridine-2-carbaldehyde), BNAH, BNA^+, and the resulting alkoxides to zinc, i.e., substrate, cofactor, and product inhibition. This situation has been investigated and discussed in detail by Ohno[37]and Engbersen.[38] The complications involved are also the reason for taking the initial rates only, and they have inhibited us from undertaking a more detailed kinetic study.

The observations nevertheless lead to a consistent interpretation. First, the fact that the reduction of pentafluorobenzaldehyde is accelerated three times as much as that of pyridine-2-carbaldehyde is an expression of substrate inhibition. Pyridine-2-carbaldehyde forms the stable complex **8** in which the ability of zinc to activate the aldehyde function is obviously reduced. Second the leveling off of the catalytic activity at higher concentrations of **5** is an expression of product inhibition. The resulting electron-poor alkoxides are suitable ligands for zinc, and we have already prepared the complex $Tt^{Me}Zn-OCH_2C_6F_5$.[27] Performing the BNAH reduction of pentafluorobenzaldehyde with 5 mM concentrations of all reagents led to a product mixture in which the major species $Tt^{t-Bu}Zn-OCH_2C_6F_5$ was identified by ^1H and ^{19}F NMR. Third, the observed initial rates are an indication of the quality of the catalyst **5**, being a closer representation of the enzyme than the previously used zinc complexes.[35,37,38] The catalytic rate enhancements (up to 6-fold for pentafluorobenzaldehyde and up to 2.5-fold for pyridine-

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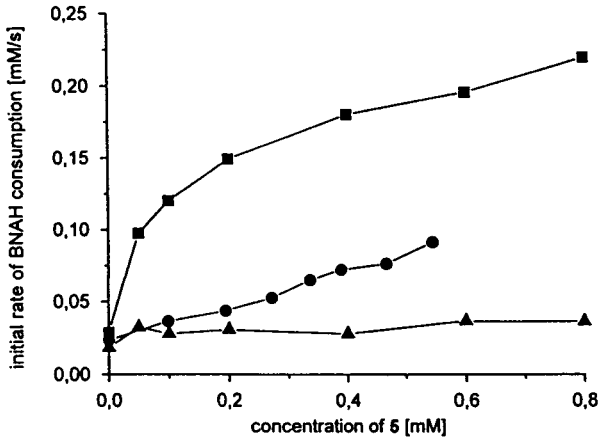

Figure 10. Initial rates of BNAH consumption as a function of the concentration of **5** at 50 °C in methanol. Triangles: in the absence of aldehydes. Circles: in the presence of pyridine-2-carbaldehyde. Squares: in the presence of pentafluorobenzaldehyde.

2-carbaldehyde) are equal to or better than the rate enhancements observed for similar reactions before.

Conclusions

The two new tris(2-thioimidazolyl)hydroborate (Tt) ligands used in this work have enabled new insights in the field of sulfur-rich coordination compounds of zinc and their biomimetic chemistry. They are reliable tetrahedral enforcers, and the propeller-like arrangement of the three thioimidazole planes in the TtZn complexes allows for a much better adherance of the ZnS_3X centers to tetrahedral geometry than is the case for the ZnN_3X centers in tris(pyrazolyl)hydroborato zinc complexes. It is noteworthy that the soft ZnS_3 units go along very well with hard donors (F, O, N) on the fourth coordination site.

The emphasis of this work was on compounds, structures, and reactions related to the properties of the sulfur-rich reaction center of the zinc enzyme horse liver alcohol dehydrogenase. The complex $Tt^{tBu}Zn-OClO_3$ which represents a "naked" L_3-Zn reaction center was found to be a key intermediate. It has enabled the attachment of ethanol, alkoxides, and aldehydes to zinc, i.e., all three substrate and product types of the catalytic chemistry of alcoholdeyhdrogenase. This is the first time that this has been achieved for the same ZnL_n unit. Thereby the thioimidazolylborate zinc complexes have shown their potential as a complement of the pyrazolylborate zinc complexes. The latter are ideal for modeling enzymatic hydrolysis reactions,[24] the former seem to be the right ones for modeling structure and function of alcohol dehydrogenase. Using the TtZn complexes as catalysts, both the oxidation of 2-propanol to acetone by BNA^+ and the reduction of electron-poor aldehydes to the corresponding alkoxides by BNAH could be perfomed. Up to 6-fold rate enhancements could be achieved for the reductions, and the complex kinetic behavior could be related to substrate and product inhibition. Although the rate enhancements are among the best observed so far for reactions of this type, they are still poor in comparison to the enzyme.

Thus the results of this work are still only another step upward on the ladder to a good alcoholdeydrogenase model. The essential TtZn·substrate complexes of this paper have a ZnS_3O coordination and one positive charge. There remains the challenge to find a tridentate ligand which allows the formation and interconversion of ZnS_2N·substrate complexes which are uncharged, as is the case in the enzyme. Like Parkin and coworkers[21] we have recently made one step in this direction by preparing a ZnS_2N variant of the complexes described here in the form of a bis(thioimidazolyl)(pyrazolyl)hydroborate zinc-ethanol complex.[25]

Experimental Section

The general experimental procedures were as described previously.[39] The reagents *N-tert*-butyl-2-thioimidazole[40] and *N*-4-cumenyl-2-thioimidazole[41] were prepared according to the published procedures. The preparations of the K[Tt] salts required completely anhydrous conditions.

Warning: Perchlorate salts of metal-organic compounds are potentially hazardous and should be used with appropriate precaution.

K[Tt^{t-Bu}]. *N-tert*-butyl-2-thioimidazole (7.67 g, 49.1 mmol) and finely ground KBH_4 (882 mg, 16.4 mmol) were suspended in 50 mL of toluene and heated to reflux for 4 days. The resulting precipitate was filtered off, washed with toluene, dried in vacuo and recrystallized from ethyl acetate/cyclohexane (1:1), yielding 4.91 g (51%) of K[Tt^{t-Bu}] as a colorless powder, mp 180 °C, which loses ethyl acetate upon prolonged pumping.

Anal. Calcd for $C_{21}H_{34}BKN_6S_3 \cdot C_4H_8O_2$ (M_r = 516.7 + 88.1): C, 49.65; H, 7.00; N, 13.90; S, 15.91. Found: C, 48.36; H, 7.10; N, 13.87; S, 15.90. IR (KBr): $\tilde{\nu}$ (BH) at 2554 (w) cm^{-1}. ^1H NMR (CD_3OD): δ 1.79 [s, 27H, *t*-Bu], 6.10 [d, J = 2.0 Hz, 3H, H^5], 6.95 [d, J = 2.0 Hz, 3 H, H^4].

K(Tt^{Cum}]. *N*-4-cumenyl-2-thioimidazole (13.1 g, 60.0 mmol) and finely ground KBH_4 (1.08 g, 20.0 mmol) were suspended in 120 mL of toluene and heated to reflux for 5 days. After cooling to 60 °C, filtration, washing with toluene and drying in vacuo 12.5 g (89%) of K[Tt^{Cum}] remained as a colorless powder, mp 216 °C (dec). Anal. Calcd. for $C_{36}H_{40}BKN_6S_3$ (M_r = 702.9): C, 61.52; H, 5.74; N, 11.96; S, 13.69. Found: C, 61.38; H, 5.83; N, 11.65; S, 13.40. IR (KBr): $\tilde{\nu}$ (BH) at 2516(w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.25 [d, J = 6.9 Hz, 18H, Me-(i-Pr)], 2.93 [sept., J = 6.9 Hz, 3H, H(i-Pr)], 6.38 [d, J = 2.2 Hz, 3H, H^5], 6.84 [d, J = 2.2 Hz, 3H, H^4], 7.28 [d, J = 8.3 Hz, 6H, $Ph^{3,5}$], 7.48 [d, J = 8.3 Hz, 6H, $Ph^{2,6}$].

Complex 1. $ZnCl_2$ (65 mg, 0.48 mmol) in methanol (10 mL) were added to K[Tt^{t-Bu}] (0.25 g, 0.48 mmol) in methanol (4 mL). Within a few minutes, 0.26 g (92%) of **1** had precipitated as colorless needles, mp 249 °C (dec), which were filtered off, washed with methanol, and dried in vacuo.

Anal. Calcd. for $C_{21}H_{34}BClN_6S_3Zn$ (M_r = 578.4): C, 43.61; H, 5.92; N, 14.53; S, 16.63; Zn, 11.31. Found: C, 43.89; H, 6.02; N, 14.51; S, 16.68; Zn, 11.00. IR (KBr): $\tilde{\nu}$ (BH) at 2421(w) cm^{-1}. ^1H NMR (CD_3CN): δ 1.72 [s, 27H, *t*-Bu], 6.90 [d, J = 2.3 Hz, 3H, H^5], 7.16 [d, J = 2.3 Hz, 3H, H^4].

Complex 2. To a solution of K[Tt^{t-Bu}] (100 mg, 0.19 mmol) in methanol (6 mL) were added solutions of $Zn(NO_3)_2 \cdot 4H_2O$ (50 mg, 0.19 mmol) and KF (11 mg, 0.19 mmol) in 4 mL of methanol each. Upon addition of CCl_4 (30 mL) a precipitate was formed which was filtered off after 30 min. The filtrate was evaporated to dryness and the residue recrystallized from ethanol/acetonitrile (1:1), yielding 84 mg (80%) of **2** as colorless crystals, mp 238 °C.

Anal. Calcd. for $C_{21}H_{34}BFN_6S_3Zn$ (M_r = 561.9): C, 44.89; H, 6.10; N, 14.96; S, 17.12; Zn, 11.64. Found: C, 44.89; H, 6.11; N, 14.82; S, 17.57; Zn, 11.70. IR (KBr): $\tilde{\nu}$ (BH) at 2429(w) cm^{-1}. ^1H NMR (CD_3OD): δ 1.76 [s, 27H, *t*-Bu], 6.96 [d, J = 2.3 Hz, 3H, H^5], 7.28 [d, J = 2.3 Hz, 3H, H^4]. ^{19}F NMR (CD_3OD): δ −180.0 (br).

Complex 3. $Zn(NO_3)_2 \cdot 4H_2O$ (65 mg, 0.48 mmol) in ethanol (10 mL) was added with stirring to K[Tt^{t-Bu}] (0.25 g, 0.48 mmol) in ethanol (15 mL). The resulting precipitate was filtered off and the filtrate reduced to 1 mL in vacuo. The precipitated solid was filtered off, washed with 0.5 mL of ethanol, and dried in vacuo, yielding 0.26 g (92%) of **3** as colorless crystals, mp 230 °C.

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Anal. Calcd. for $C_{21}H_{34}BN_7O_3S_3Zn$ (M_r = 604.9): C, 41.69; H, 5.66; N, 16.21; S, 15.90; Zn, 10.81. Found: C, 41.38; H, 5.57; N, 16.08; S, 15.22; Zn, 10.72. IR (KBr): $\tilde{\nu}$ (BH) at 2479(w) cm^{-1}. ^1H NMR (CD_3OD): δ 1.76 [s, 27H, *t*-Bu], 7.01 [d, J = 2.4 Hz, 3H, H^5], 7.32 [d, J = 2.4 Hz, 3H, H^4].

Complex 4. $Zn(ClO_4)_2 \cdot 6H_2O$(146 mg, 0.39 mmol) in methanol (5 mL) was added quickly with stirring to K[$Tt^{t\text{-}Bu}$] (400 mg, 0.78 mmol) in methanol (5 mL). The precipitate was filtered off, the filtrate reduced to 3 mL in vacuo, and the solution filtered again. The remaining filtrate was evaporated to dryness and the residue recrystallized from dichloromethane/hexane (1:2), yielding 308 mg (77%) of **4** as colorless crystals, mp 224 °C (dec)

Anal. Calcd. for $C_{42}H_{68}B_2N_{12}S_6Zn$ (M_r = 1020.5): C, 49.43; H, 6.72; N, 16.47; S, 18.85; Zn, 6.41. Found: C, 50.27; H, 7.15; N, 14.71; S, 17.18; Zn, 6.15. IR (KBr): $\tilde{\nu}$ (BH) at 2503 (w) cm^{-1}. ^1H NMR (CD_3OD): δ 1.74 [s, 27H, *t*-Bu], 6.98 [br, 6H, H^5], 7.06 [br, 6H, H^4].

Complex 5. A solution of K[$Tt^{T\text{-}Bu}$] (200 mg, 0.39 mmol) in methanol (15 mL) was added dropwise with stirring within 20 min to a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (144 mg, 0.39 mmol) in methanol (15 mL). The volume of the solution was reduced to 15 mL in vacuo, the precipitate was filtered off, and the filtrate evaporated to dryness. The residue was taken up in 10 mL of dichloromethane, filtered, and evaporated to dryness again, 193 mg (76%) of **5** remained as a colorless powder, mp 248 °C (dec).

Anal. Calcd. for $C_{21}H_{34}BClN_6O_4S_3Zn$ (M_r = 642.4): C, 39.26; H, 5.33; N, 13.08; S, 14.98; Zn, 10.18. Found: C, 39.87; H, 5.31; N, 12.23; S, 14.40; Zn, 10.07. IR (KBr): $\tilde{\nu}$ (BH) at 2426(w), $\tilde{\nu}$ (ClO_4) at 1121(s), 1109(s) and 1090(s) cm^{-1}. ^1H NMR (CD_3CN): δ 1.73 [s, 27H, *t*-Bu], 6.97 [d, J = 2.2 Hz, 3H, H^5], 7.23 [d, J = 2.2 Hz, 3H, H^4].

Complex 6. A solution of K[$Tt^{t\text{-}Bu}$] (200 mg, 0.39 mmol) in ethanol (15 mL) was added dropwise with stirring within 20 min to a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (144 mg, 0.39 mmol) in ethanol (15 mL). The resulting precipitate was filtered off. Addition of 50 mL of hexane to the filtrate produced a precipitate which was filtered off and dried in vacuo. A total of 233 mg (82%) of **6** remained as a colorless powder, mp 126 °C (dec).

Anal. Calcd. for $C_{25}H_{46}BClN_6O_6S_3Zn$ (M_r = 734.5): C, 40.88; H, 6.31; N, 11.44; S, 13.10; Zn, 8.90. Found: C, 40.60; H, 6.23; N, 11.63; S, 13.19; Zn, 9.20. IR (KBr): $\tilde{\nu}$ (BH) at 2429(w), $\tilde{\nu}$ (ClO_4) at 1110(s) cm^{-1}. ^1H NMR (CD_3CN): δ 1.12 [t, J = 7.0 Hz, 6H, CH_3], 1.73 [s, 27H, *t*-Bu], 2.42 [t, J = 5.2 Hz, 2H, OH], 3.54 [dt, J = 7.0 and 5.2 Hz, 4H, CH_2], 6.97 [d, J = 2.3 Hz, 3H, H^5], 7.23 [d, J = 2.3 Hz, 3H, H^4].

Complex 7. A solution of K[Tt^{Cum}] (206 mg, 0.33 mmol) in dichloromethane (5 mL) was added with stirring to a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (140 mg, 0.38 mmol) in methanol (10 mL). After stirring for 2 h a solution of KOC_6H_4-*p*-NO_2 (56 mg, 0.33 mmol) in methanol (10 mL) was added and the mixture stirred for another 24 h. After evaporation to dryness the residue was extracted with dichloromethane and separated from the insoluble parts by filtration and the filtrate was evaporated to dryness again and the residue recrystallized from dichloromethane/acetontrile (1:1) yielding 196 mg (69%) of **7** as yellow crystals, mp 231 °C (dec), which were freed from cocrystallized solvent by prolonged pumping.

Anal. Calcd. for $C_{42}H_{44}BN_7O_3S_3Zn$ (M_r = 867.3): C, 58.17; H, 5.11; N, 11.31; S, 11.09; Zn, 7.54. Found: C, 58.18; H, 5.17; N, 11.50; S, 11.57; Zn, 7.37. IR (KBr): $\tilde{\nu}$ (BH) at 2412(w), $\tilde{\nu}$ (NO_2) at 1295(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.28 [d, J = 7.0 Hz, 18H, Me(i-Pr)], 2.99 [sept., J = 6.8 Hz, 3H, H(i-Pr)], 6.31 [d, J = 5.2 Hz, 2H, $PhNO_2^{3,5}$], 7.11 [d, J = 2.2 Hz, 3H, H^5], 7.17 [d, J = 2.2 Hz, 3H, H^4], 7.28 [d, J = 8.6 Hz, 6H, $Cum^{2,6}$], 7.37 [d, J = 8.6 Hz, 6H, $Cum^{3,5}$], 7.74 [d, J = 5.2 Hz, 2H, $PhNO_2^{2,6}$].

Complex 8. A solution of PyCHO (33 mg, 0.31 mmol) in chloroform (5 mL) was added with stirring to a suspension of **5** (0.20 g, 0.31 mmol) in chloroform (10 mL). A clear solution resulted. Addition of 20 mL of hexane precipitated 0.21 g (90%) of **8** as a yellow powder, mp 136 °C, which was filtered off, washed with hexane, and dried in vacuo.

Anal. Calcd. for $C_{27}H_{39}BClN_7O_5S_3Zn$ (M_r = 749.5): C, 43.27; H, 5.24; N, 13.08; S 12.83; Zn, 8.72. Found: C, 43.23; H, 5.02; N, 12.43; S, 11.88; Zn, 8.41. IR (KBr): $\tilde{\nu}$ (BH) at 2424(w), $\tilde{\nu}$ (CO) at 1715(m), $\tilde{\nu}$ (Py) at 1602(m), $\tilde{\nu}$ (ClO_4) at 1096(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.75 [s, 27H, *t*-Bu], 6.87 [d, J = 2.0 Hz, 3H, H^5], 7.06 [d, J = 2.0 Hz, 3H, H^4], 7.65 [m, 1H, Py], 8.08 [m, 1H, Py], 8.90 [m, 1H, Py], 10.10 [s, 1H, CHO].

Complex 9. Potassium 2-formylphenolate (50 mg, 0.31 mmol) was added to a suspension of **5** (0.20 g, 0.31 mmol) in dichloromethane (10 mL) and the mixture stirred for 1 day. After filtration the filtrate was evaporated to dryness, leaving behind 0.16 g (78%) of **9** as a yellow powder, mp 78 °C.

Anal. Calcd. for $C_{28}H_{39}BN_6O_2S_3Zn \cdot 0.5CH_2Cl_2$ (M_r = 664.1 + 42.5): C, 48.45; H, 5.71; N, 11.89; S, 13.62; Zn, 9.26. Found: C, 48.48; H, 5.62; N, 11.93; S, 13.21; Zn, 9.67. IR (KBr): $\tilde{\nu}$ (BH) at 2425(w), $\tilde{\nu}$ (CO) at 1659(m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.77 [s, 27H, *t*-Bu], 5.35 [s, 1H, CH_2Cl_2], 6.83 [d, J = 2.2 Hz, 3H, H^5], 7.00 [d, J = 2.2 Hz, 3H, H^4], 7.07 [m, 2H, $Ph^{3,5}$], 7.49 [m, 2H, $Ph^{4,6}$], 9.90 [s, 1H, CHO].

Complex 10a. A solution of $PyCH_2OH$ (34 mg, 0.31 mmol) in methanol (15 mL) was added with stirring within 30 min to a solution of **5** (0.20 g, 0.31 mmol) in methanol (15 mL). After another 30 min the solvent was removed in vacuo and the residue taken up in 20 mL of chloroform and filtered. Addition of 30 mL of hexane to the filtrate precipitated 0.19 g (39%) of **10a** as a colorless powder, mp 172 °C (dec), which was washed with hexane and dried in vacuo.

Anal. Calcd. for $C_{54}H_{80}B_2Cl_2N_{14}O_{10}S_6Zn_3$ (M_r = 1566.4): C, 41.41; H, 5.15; N, 12.52; S, 12.28; Zn, 12.52. Found: C, 41.21; H, 5.45; N, 12.77; S, 12.62; Zn, 12.48. IR (KBr): $\tilde{\nu}$ (BH) at 2448(w), $\tilde{\nu}$ (ClO_4) at 1109(s) cm^{-1}. ^1H NMR (CD_3OD): δ 1.76 [s, 27H, *t*-Bu], 4.65 [s, 2H, CH_2O], 7.02 [d, J = 2.3 Hz, 3H, H^5], 7.33 [dd, J = 4.6 and 6.9 Hz, 1H, Py^5], 7.34 [d, J = 2.3 Hz, 3H, H^4], 7.57 [d, J = 7.7 Hz, 1H, Py^3], 7.87 [dd, J = 6.9 and 7.7 Hz, 1H, Py^4], 8.48 [d, J = 4.6 Hz, 1H, Py^6].

Complex 10b. Prepared like **10a** from $MePyCH_2OH$ (38 mg, 0.31 mmol) and **5** (0.20 g, 0.31 mmol). Yield 0.17 g (34%) of **10b** as colorless crystals, mp 158 °C (dec).

Anal. Calcd. for $C_{56}H_{84}B_2Cl_2N_{14}O_{10}S_6Zn_3$ (M_r = 1594.5): C, 42.18; H, 5.31; N, 12.30; S, 12.07; Zn, 12.30. Found: C, 41.58; H, 5.30; N, 11.97; S, 11.45; Zn, 11.96. IR (KBr): $\tilde{\nu}$ (BH) at 2486(w), $\tilde{\nu}$ (ClO_4) at 1094(s) cm^{-1}. ^1H NMR (CD_3OD): δ 1.76 [s, 27H, *t*-Bu], 2.53 [s, 3H, CH_3], 4.68 [s, 2H, CH_2O], 7.02 [d, J = 2.3 Hz, 3H, H^5], 7.21 [d, J = 7.8 Hz, 1H, Py^5], 7.34 [d, J = 2.3 Hz, 3H, H^4], 7.38 [d, J = 7.8 Hz, 1H, Py^3], 7.78 [dd, J = 7.8 and 7.8 Hz, 1H, Py^4].

Oxidation of 2-Propanol. A total of 200 μL (156 mg, 2.60 mmol) of water-free 2-propanol were added to a solution of 43.4 mg (0.050 mmol) of **7** and 12.5 mg (0.050 mmol) of [BNA]Cl in 2.0 mL of water-free $(CD_3)_2SO$. The mixture was stirred for 24 h in the dark. ^1H NMR spectroscopy showed the appearance of acetone (δ = 2.08) and BNAH (δ = 4.30 for the benzyl protons), while BNA^+ (δ = 5.98 for the benzyl protons) was consumed.

Reduction of Pentafluorobenzaldehyde. C_6F_5CHO (10 mg, 0.05 mmol), **5** (32 mg, 0.05 mmol) and BNAH (9 mg, 0.05 mmol) in 2 mL of acetonitrile were stirred at 50 °C for 1 h. The solvent was removed in vacuo, the residue extracted with dichloromethane and the extract evaporated to dryness, leaving behind 30 mg (75%) of impure $Tt^{t\text{-}Bu}Zn{-}OCH_2C_6F_5$.

^1H NMR (CD_3CN): δ 1.73 [s, 27H, *t*-Bu], 4.33 [s, 2H, CH_2], 6.97 [d, J = 2.3 Hz, 3H, H^5], 7.23 [d, J = 2.3 Hz, 3H, H^4]. ^{19}F NMR (CD_3CN): δ −144.6 [m, 2F, $F^{3,5}$], −159.4 [m, 1F, F^4], −164.7 [m, 2F, $F^{2,6}$].

Kinetic Measurements. A Jasco V-570 UV−vis spectrometer was used to continuously monitor the 348 nm absorption of BNAH. The acetonitrile solutions of the aldehydes, complex **5**, and BNAH were brought to 50 °C before the measurements which were performed at 50 °C. In the combined solutions the concentration of the aldehydes was 2.0 mM, of BNAH 0.20 mM and of **5** 0−1.8 mM. The reactions were followed for 600 s, the initial rates were computed using the data of the first 100 s. The measurements could be reproduced with 95% precision. A slow decay of the BNAH absorption was observed even in the absence of the aldehydes, and it showed a very small dependence on the concentration of **5**, cf. Figure 10.

Table 1. Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{21}H_{34}BClN_6S_3Zn\cdot CH_3CN$	$C_{21}H_{34}BFN_6S_3Zn$	$C_{21}H_{34}BN_7O_3S_3Zn$	$C_{42}H_{68}B_2N_{12}S_6Zn\cdot 3CH_2Cl_2$
MW	578.4 + 41.1	561.9	604.9	1020.5 + 254.8
space group	*Fdd*2	*R*3*c*	$P2_1/n$	*C*2/*c*
Z	16	6	4	8
a (Å)	35.322(2)	11.515(2)	11.044(1)	40.017(5)
b (Å)	35.523(2)	11.515(2)	15.893(1)	11.387(1)
c (Å)	9.540(1)	37.362(8)	16.039(1)	29.230(4)
α (deg)	90	90	90	90
β (deg)	90	90	90.098(2)	110.540(4)
γ (deg)	90	120	90	90
V (Å^3)	11970(1)	4290(1)	2815.1(4)	12473(3)
d calcd (g cm^{-3})	1.38	1.31	1.43	1.36
μ Mo Kα (mm^{-1})	1.15	1.10	1.13	0.89
R1 (obs reflns)[a]	0.037	0.145	0.039	0.050
wR2 (all reflns)[a]	0.147	0.381	0.090	0.130

	5	**6**	**7**	**10b**
formula	$C_{21}H_{34}BClN_6O_4S_3Zn$	$C_{25}H_{46}BClN_6O_6S_3Zn$	$C_{46}H_{47}BN_8O_3S_3Zn$	$C_{56}H_{84}B_2Cl_2N_{14}O_{10}S_6Zn_3\cdot C_6H_{14}\cdot 3CH_2Cl_2$
MW	642.4	734.5	908.3	1594.5 + 342.9
space group	$P2_1/n$	*C*2/*c*	$P\bar{1}$	$P2_1/c$
Z	4	8	2	4
a (Å)	11.031(2)	25.343(2)	11.287(2)	16.604(4)
b (Å)	16.314(3)	19.627(2)	14.434(2)	23.950(5)
c (Å)	16.093(3)	18.512(2)	15.777(2)	23.153(5)
α (deg)	90	90	66.776(2)	90
β (deg)	90.28(3)	126.968(2)	72.317(3)	108.188(4)
γ (deg)	90	90	84.854(3)	90
V (Å^3)	2896(1)	7357(1)	2249.1(5)	8747(3)
d calcd (g cm^{-3})	1.47	1.33	1.34	1.47
μ Mo Kα (mm^{-1})	1.20	0.95	0.73	1.26
R1 (obs reflns)[a]	0.038	0.040	0.108	0.061
wR2 (all reflns)[a]	0.086	0.115	0.310	0.207

[a] $R1 = \sum|F_o - F_c|/\sum F_o$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Structure Determinations. Crystals of **2**, **4**, and **7** were taken as obtained from the preparations, those of **1** were obtained from ethanol/acetonitrile, of **3** by slow evaporation of a methanol solution, of **5** and **10b** by layering a dichloromethane solution with hexane, of **6** from ethanol/hexane. Several crystals of **2** produced mediocre data sets with $R_{int} > 0.3$, resulting in an unsatisfactory *R* value. In case of **3** and **6** there was disorder of the nitrate and ethanol ligands, respectively. In case of **4** and **10b** the cocrystallized solvent molecules displayed high-temperature factors, and the hexane molecule in **10b** was ill-defined.

The data sets were obtained with a Bruker AXS Smart CCD diffractometer and subjected to an empirical absorption correction. The structures were solved with direct methods and refined anisotropically using the SHELX program suite.[42] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. Drawings were produced with SCHAKAL.[43] Table 1 lists the crystallographic data.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. We thank Drs. R. Walz and B. Wu for preparative contributions and Drs. A. Trösch, H. Brombacher and B. Kersting for X-ray work.

Supporting Information Available: Fully labeled ORTEP plots and X-ray crystallographic files in CIF format for the eight structure determinations.This material is available free of charge via the Internet at http://pubs.acs.org.

IC0101275

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