Zinc Pyrazolylborate Complexes with Phenoxide and Alkoxide Ligands☆

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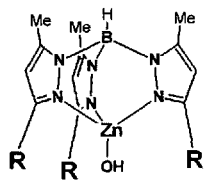
The zinc hydroxide complexes Tp*Zn−OH of highly substituted pyrazolylborate ligands react with phenols, and alcohols, of sufficient acidity, in a condensation reaction with release of H_2O. Starting with phenols the following were attached: phenolate, *p*-nitrophenolate, *o*-vanillinate, *o*-hydroxymethylphenolate, *o*,*o*-bis(hydroxymethyl)-*p*-methylphenolate. Whilst aliphatic alcohols and benzyl alcohol did not react, their derivatives, with highly electronegative substituents, could be incorporated. Thus, the arylmethoxides $OCH_2C_6F_5$ and $OCH_2C_6H_4NO_2$-*p*, as well as the alkoxides OCH_2CF_3 and OCH_2CCl_3, were attached. 2-Mercaptoethanol was bound via its thiolate function. The crystal structures of $Tp^{Cum,Me}Zn-OC_6H_4NO_2$-*p*, $Tp^{Cum,Me}Zn-OCH_2-C_6F_5$, $Tp^{Cum,Me}Zn-OCH_2CF_3$, $Tp^{Cum,Me}Zn-OCH_2CCl_3$ and $Tp^{Cum,Me}Zn-SCH_2CH_2OH$ were determined.

There are two motivations behind the search for zinc complexes with terminal alkoxide ligands. One of them is the renewed interest in metal alkoxides in general[1−3], particularly as intermediates in the preparation of new metal oxide materials[4]. The other is the occurrence of zinc in the active center of the enzyme horse liver alcohol dehydrogenase[5,6]. In both cases a modelling of the technical or biological processes involved requires the investigation of zinc complexes with terminal alcohol or alkoxide ligands as the starting points of the reaction sequences.

A review of the literature shows that there are a few scattered examples of zinc complexes containing, among their ligands, alcohol molecules[7]. But whilst zinc-containing species with bridging phenoxide or alkoxide ligands are commonplace, and while there are a considerable number of complexes containing a zinc ion attached to an (N,O) chelate ligand containing the O donor as an alkoxide function[1−4,8], Zn−OR units with terminal OR groups seem to be extremely rare. Tetraalkoxozincates are known[8], but none of them seem to have been characterized by a structure determination. In the literature[8−10], and in the Cambridge Crystallographic Data File, we found two zinc methoxide complexes with macrocyclic ligands mentioned[11,12], one of which is said to have been the subject of an X-ray analysis[12]. Similarly, the complex $Tp^{iPr,iPr}Zn-OC_6H_4-NO_2$-*p*, which is also said to have been structurally characterized, was mentioned in a short communication[13]. Only one structure of a zinc complex containing terminal alkoxide groups, $Na_2[Zn_2(OtBu)_6]$[14], seems to have been reported in the open literature. On this basis it must be considered remarkable that the structures of the enzyme alcohol dehydrogenase, containing the non-productive pseudosubstrates pentafluorobenzyl alcoholate and *p*-bromobenzyl alcoholate, are known[15].

Mononuclear zinc complexes with alkoxide ligands came to our attention when studying Tp*Zn−OH/CO_2 reactions in terms of modelling the enzyme carbonic anhydrase[16], or for catalytic conversions of CO_2 to dialkyl carbonates[17]. We observed that the highly labile species Tp*Zn−OMe and Tp*Zn−OEt seem to be related to CO_2 release from Tp*Zn−OCOOR, or CO_2 absorption by Tp*Zn−OH in alcoholic solution. When modelling the chemistry of zinc-containing phosphatases[18,19], we found the nitrophenolate complexes Tp*Zn−$OC_6H_4NO_2$-*p* to be among the products of cleavage of phosphoric acid nitrophenolate esters by Tp*Zn−OH. Furthermore, when modelling the hydride abstraction from alcohols with formation of aldehydes as catalyzed by the zinc enzyme horse liver alcohol dehydrogenase, one wishes to have terminal zinc alkoxide complexes as substrates for alcohol oxidation.

With this in mind we investigated the possibilities of obtaining Zn−OR complexes from the reaction between Tp*Zn−OH and alcohols or phenols, based on the experience that the OH ligand is easily replaced by the anions of even very weak acids[16,19−22]. The Tp*Zn−OH complexes used were **1a−c**, bearing substituents of varying steric bulk in the 3-position. The organic OH compounds used as reagents were phenol, benzyl alcohol, and ethanol, as well as derivatives thereof with electronegative substituents. The interconversions proceeded either not at all, or swiftly, in dichloromethane under anhydrous conditions.



1a ($Tp^{tBu,Me}$Zn-OH) : R = t-Bu

1b ($Tp^{Ph,Me}$Zn-OH) : R = Ph

1c ($Tp^{Cum,Me}$Zn-OH): R = C_6H_4-*p*-*i*Pr (Cumenyl)

Phenolates

Every phenol derivative used could be incorporated, in good yields, in the phenolate complexes **2a−e**. They are

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colourless crystalline solids, with the exception of the *p*-nitrophenolates which are yellow. We were able to identify the latter **2b$_1$**, **2b$_2$**, **2b$_3$** for all three pyrazolylborate ligands; they were observed regularly as cleavage products of *p*-nitrophenyl esters in our mechanistic studies[18]. The phenols with *o*-hydroxymethyl and *o*-formyl substituents were used with the purpose of bringing their alcoholic or aldehydic functions into the vicinity of the zinc ion, such as to condition them for subsequent catalytic hydrogenation or dehydrogenation reactions. All complexes (**2** as well as **3**–**5**, see below) show the typical IR bands (OH, BH, NO, ring vibrations) and a full set of ^{1}H-NMR resonances (see Experimental Section). The structure of **2b$_1$** was determined (see below). In case of complex **2c** (vanillinate) a slight shift of the aldehydic CO vibration (from 1669 cm^{-1} in the free phenol to 1661 cm^{-1} in the complex) indicates the possibility of a weak coordination of the aldehydic function to the zinc ion.

$Tp^{Cum,Me}Zn\text{-}OC_6H_5$
2a

$Tp^{Cum,Me}Zn\text{-}OC_6H_4\text{-}p\text{-}NO_2$
2b$_1$

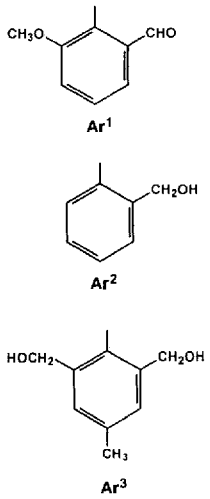
$Tp^{Ph,Me}Zn\text{-}OC_6H_4\text{-}p\text{-}NO_2$
2b$_2$

$Tp^{tBu,Me}Zn\text{-}OC_6H_4\text{-}p\text{-}NO_2$
2b$_3$

$Tp^{Cum,Me}Zn\text{-}O\text{-}Ar^1$
2c

$Tp^{Cum,Me}Zn\text{-}O\text{-}Ar^2$
2d

$Tp^{Cum,Me}Zn\text{-}O\text{-}Ar^3$
2e



Arylmethoxides

Benzyl alcohol and its derivatives are less acidic than phenols, but we found that they are still reactive towards the Zn–OH complexes **1**. Benzyl alcohol, however, reacted sluggishly, and we could not isolate a pure arylmethoxide complex. Such problems did not exist for *p*-nitrobenzyl alcohol or pentafluorobenzyl alcohol which easily produced complexes **3a** and **b**. To confirm this **3b$_1$** was subjected to a structure determination (see below).

$Tp^{Cum,Me}Zn\text{-}O\text{-}CH_2C_6H_4\text{-}p\text{-}NO_2$
3a

$Tp^{Cum,Me}Zn\text{-}O\text{-}CH_2C_6F_5$
3b$_1$

$Tp^{tBu,Me}Zn\text{-}O\text{-}CH_2C_6F_5$
3b$_2$

Alkoxides

From the very fact that the Zn–OH complexes **1** can best be brought to reaction in methanol/dichloromethane mixtures it was clear that they do not react with simple alcohols, and correspondingly their simple alkoxide derivatives are quickly destroyed by hydrolysis[16,17]. We now found, however, that trifluoroethanol and trichloroethanol are sufficiently acidic to be incorporated and form complexes **4** which were both verified by structure determinations (see below).

We already knew that the chelate effect can stabilize Tp*Zn–alkoxide-like species, e.g. in the form of hydroxyacetone derivatives[21]. Therefore we had hoped that Zn(S,O) chelation might support the formation of an alkoxide complex derived from β-mercaptoethanol. The experiment, however, showed that the thiophilicity of zinc prevails, and that the simple thiolate complex **5** is the only reaction product. Proof for this was again obtained from a structure determination (see below).

$Tp^{Cum,Me}Zn\text{-}O\text{-}CH_2CF_3$
4a

$Tp^{Cum,Me}Zn\text{-}O\text{-}CH_2CCl_3$
4b

$Tp^{Cum,Me}Zn\text{-}S\text{-}CH_2CH_2OH$
5

Structure Determinations

The results of the five structure determinations are depicted in Figures 1–5. In all cases the expected pseudo-tetrahedral coordination of the zinc ion by the tridentate pyrazolylborate and the monodentate coligand was found. The trichloroethanolate complex **4b** crystallizes in the trigonal space group *P*-3 with the pyrazolylborate ligand located around the trigonal axis, which implies threefold disorder of the trichloroethyl group thereby making its structural details uncertain. The significant bonding parameters of the four complexes with a ZnN_3O coordination are summarized in Table 1.

The central cores of all four complexes with a ZnN_3O coordination are quite similar, cf. Table 1. The oxygen atom lies very close to the trigonal axis of the Tp*Zn unit, and the Zn–O–C connection is bent with an angle well beyond the tetrahedral value. The latter may be related to the encapsulation which forces the organic group attached to the oxygen atom into the center of the molecule, but may also be due to the partly ionic nature of the Zn–O bond. The Zn–N and C–O bond lengths are in their expected ranges. The Zn–O bonds lengths are among the shortest observed. They are shorter than those in the corresponding Zn–OH[22,23] or Zn–carboxylate complexes[16,20,22]. For comparison, the only other structurally characterized zinc complex with terminal alkoxide ligands has Zn–O bond lengths of 1.89 and 1.90 Å[14].

Complex **5** can be classified as a normal Tp*Zn–thiolate complex. Its Zn–S bond length corresponds to those in

Figure 1. Molecular structure of the *p*-nitrophenolate complex **2b$_1$**

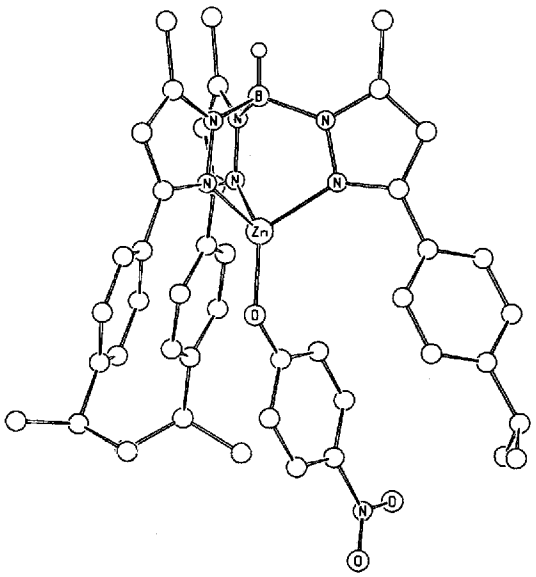


Figure 2. Molecular structure of the pentafluorobenzylate complex **3b$_1$**

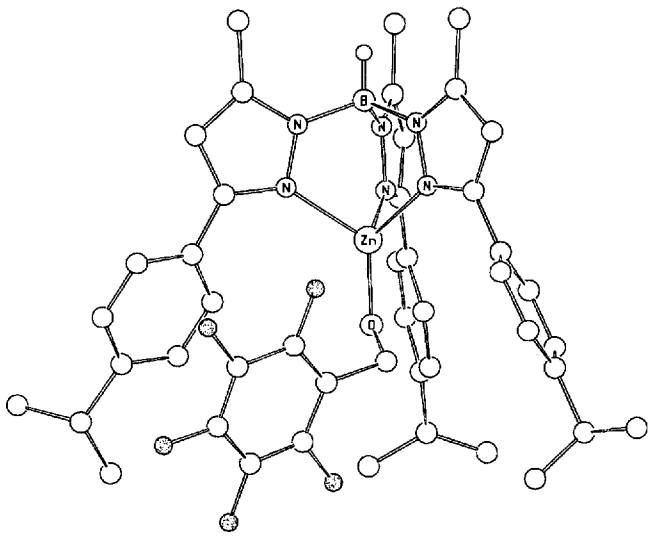


Figure 3. Molecular structure of the trifluoroethylate complex **4a**

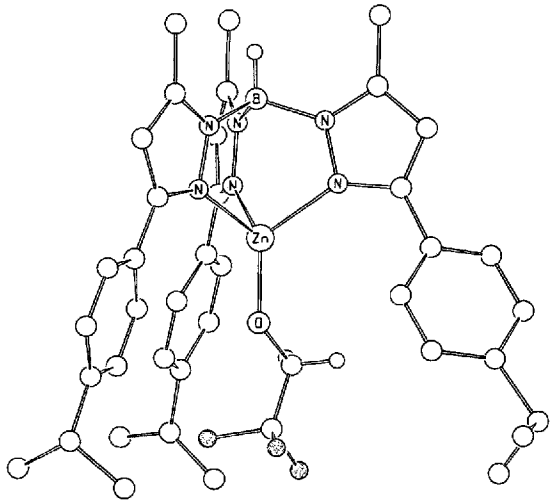
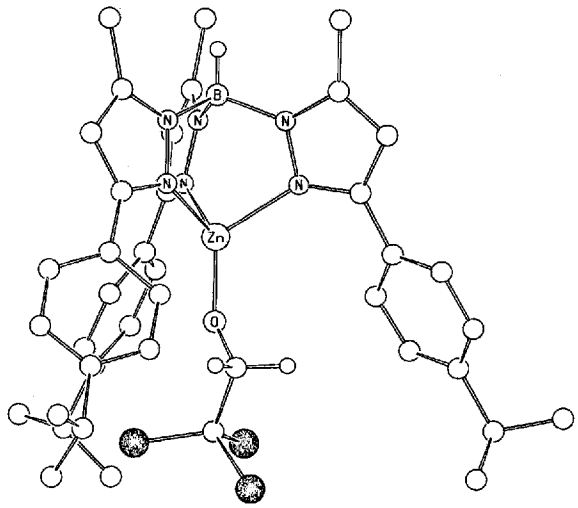


Figure 4. Molecular structure of the trichloroethylate complex **4b**



$Tp^{Ph}Zn$–SEt (2.20 Å[24]) and $Tp^{Cum,Me}Zn$–SH (2.21 Å[22]). Again these values are very short when compared to Zn–S distances in other complexes. In **5** the hydroxyethyl substituent is stretched away from the Zn–S unit such that any Zn–OH interaction need not be considered. Actually the OH group is involved in a hydrogen-bond interaction with a cocrystallized methanol molecule.

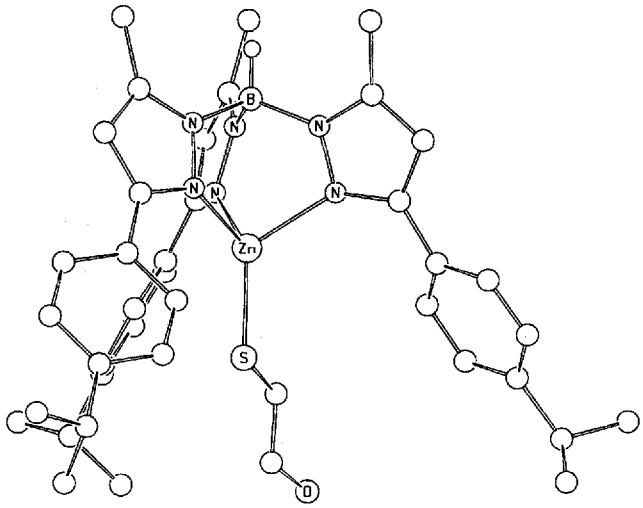
Discussion

This work is another demonstration of the value of the Tp*Zn–OH complexes as synthons. They show sufficient reactivity towards all phenols and benzyl alcohols to allow substitution of the OH ligand. They do not react with the simple alcohols, however when these bear electronegative substituents, or when they are able to become chelate ligands, reaction then occurs.

The ease of formation of the alcoholates and phenolates is seemingly in sharp contrast to the extreme senstivity of the simple alkoxides towards hydrolysis. However, apart from being a consequence of the acid-base properties of the reagents, this also indicates that the Tp*Zn–alcoholates, just like the Tp*Zn–OH complexes, may represent a very favourable combination of stability and lability. This makes the simple Tp*Zn–alkoxides attractive as reagents. Accordingly, we are working on methods of obtaining them in other ways than described by us here or previously[16,17].

The structures of the four phenoxide and alkoxide complexes give no indication as to the varying reactivity of their Zn–O functions. The Zn–O bond lengths are in accord with very strong Zn–O bonds, and there is no deviation from the common ligand arrangement. In fact, the least sensitive compound, the nitrophenolate complex **2b$_1$**, has the longest Zn–O bond. Altogether the structures demonstrate again how encapsulation by the Tp* ligands protects the labile function in the centre of the complex molecules.

Figure 5. Molecular structure of the 2-hydroxyethanethiolate complex **5**[5]



[a] Pertinent bond lengths [Å] and angle [°]: Zn–N1 2.074(3), Zn–N2 2.084(3), Zn–N3 2.086(3), Zn–S 2.223(1), S–C 1.834(5); Zn–S–C 105.5(2).

Table 1. Pertinent bond lengths [Å] and angles [°] in the zinc aryloxide and -alkoxide complexes

	2b$_1$	**3b$_1$**	**4a**	**4b**
Zn-N1	2.015(2)	2.052(3)	2.047(10)	2.048(4)
Zn-N2	2.024(2)	1.991(3)	2.048(8)	2.048(4)
Zn-N3	2.051(2)	2.034(3)	2.061(8)	2.048(4)
Zn-O	1.860(2)	1.812(2)	1.830(7)	1.815(7)
O-C	1.314(4)	1.301(5)	1.326(12)	1.29(2)
Zn-O-C	132.6(2)	122.7(3)	132.0(7)	139.0(11)

The protective effect of the Tp* ligands makes us hope that, in their enzyme-like environment, the zinc-bound alkoxides can eventually be subjected to their enzymatic interconversion, i.e. their oxidation to aldehydes by hydride abstraction. The alkoxide complexes **3** and **4** suggest themselves for these purposes, but due to their electronegative substituents they are more difficult to oxidize. It therefore remains a challenge for us to gain better access to the simple alkoxide complexes Tp*Zn–OR.

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Experimental Section

All reactions were carried out in water-free solvents under nitrogen. The general working and measuring methods are described in ref.[25], the synthesis of the Tp*Zn–OH complexes in ref.[16] and [22]. Reagents were obtained commercially.

Preparations: Starting complex **1** and the reagent were dissolved separately in dichloromethane and combined in a 100-ml flask while stirring. After the reaction time, all volatiles were removed in vacuo. The residue was picked up in the solvent of crystallization, the solution was filtered and kept in a desiccator for slow evaporation. The products remained as colourless (**2b$_1$**, **2b$_2$**, **2b$_3$** yellow), mostly crystalline solids. Table 2 lists the details of the reactions, Table 3 gives the analytical data.

^{1}H-NMR data ($CDCl_3$, int. TMS, δ):

2a: δ = 1.06 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.46 [s, 9H, Me(pz)], 2.68 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 5.92 [d, ^3J = 7.8 Hz, 2H, Phenol(3,5)], 6.07 [m, 1H, Phenol(4)], 6.08 [s, 3H, H(pz)], 6.49 [t, ^3J = 7.8 Hz, 2H, Phenol(2,6)], 6.91 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.60 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)].

2b$_1$ (Nitr = nitrophenyl): δ = 1.04 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.56 [s, 9H, Me(pz)], 2.72 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 5.75 [d, ^3J = 8.7 Hz, 2H, Nitr(2,6)], 6.24 [s, 3H, H(pz)], 7.01 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.42 [d, ^3J = 8.7 Hz, 2H, Nitr(3,5)], 7.53 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)].

2b$_2$ (Nitr = nitrophenyl): δ = 2.58 [s, 9H, Me(pz)], 5.73 [d, ^3J = 9.2 Hz, 2H, Nitr(3,5)], 6.29 [s, 3H, H(pz)], 7.15 [m, 9H, Phe(3,4,5)], 7.41 [d, ^3J = 9.2 Hz, 6H, Nitr(2,6)], 7.60 [m, 6H, Phe(2,6)].

Table 2. Reaction details

starting complex				reagent[a]				time	recryst. from	product			
no.	mg	mmol	ml	no.	mg	mmol	ml	h		no.	mg	%	m.p.
1c	200	0.289	20	A	27.2	0.289	20	2	acetonitrile	**2a**	171	77	249
1c	500	0.723	25	B	101	0.726	15	3	acetonitrile	**2b$_1$**	523	89	241
1c	200	0.289	30	C	43.9	0.289	20	4	CH_3OH/CH_2Cl_2 4:1	**2c**	168	68	229
1c	300	0.433	30	D	53.7	0.433	10	2	acetone	**2d**	219	64	177
1c	200	0.289	30	E	48.6	0.289	30	4	CH_3OH/CH_2Cl_2 4:1	**2e**	129	51	151
1b	500	0.884	30	B	123	0.884	20	3	acetonitrile	**2b$_2$**	504	83	201
1a	500	0.988	25	B	137	0.988	25	3	acetonitrile	**2b$_3$**	545	88	238
1c	200	0.289	20	F	44.3	0.289	20	20	CH_3CN/CH_2Cl_2 3:1	**3a**	165	69	171
1c	200	0.289	20	G	57.2	0.289	20	20	CH_3CN/CH_2Cl_2 4:1	**3b$_1$**	109	43	229
1a	100	0.198	40	G	39.2	0.198	20	20	CH_3CN/CH_2Cl_2 3:1	**3b$_2$**	52	34	220
1c	300	0.433	30	H	43.7	0.433	10	12	CH_3CN/CH_2Cl_2 4:1	**4a**	79	24	236
1c	200	0.289	25	I	44.0	0.289	10	1	benzene	**4b**	189	76	164
1c	200	0.289	20	J	23.0	0.289	5	1	CH_3OH/CH_2Cl_2 4:1	**5**	193	89	191

[a] A: phenol, B: *p*-nitrophenol, C: 2-methoxy-6-formylphenol (vanillin), D: 2-hydroxymethylphenol (salicylic alcohol), E: 2,6-bis(hydroxymethyl)-4-methyl phenol, F: *p*-nitrobenzyl alcohol, G: pentafluorobenzyl alcohol, H: trifluoroethanol, I: trichloroethanol, J: 2-mercaptoethanol.

Table 3. Elemental analyses

no.	formula mol. mass	calcd. found	C	H	N	Zn
2a	$C_{45}H_{51}BN_6OZn$ 768.14		70.37 69.68	6.69 6.75	10.94 10.71	
2b$_1$	$C_{45}H_{50}BN_7O_3Zn$ 813.14		66.47 65.75	6.20 6.24	12.06 12.03	
2c	$C_{47}H_{53}BN_6O_3Zn \cdot CH_3OH$ 826.18 + 32.04		67.18 66.73	6.69 6.65	9.79 9.25	7.62 7.68
2d	$C_{46}H_{53}BN_6O_2Zn$ 798.16		69.22 68.63	6.69 6.61	10.53 10.31	8.19 8.27
2e	$C_{48}H_{57}BN_6O_3Zn \cdot CH_3OH$ 842.22 + 32.04		67.32 67.25	7.03 6.92	9.61 9.29	7.48 7.62
2b$_2$	$C_{36}H_{32}BN_7O_3Zn \cdot \frac{1}{2}CH_2Cl_2$ 686.89 + 42.46		60.11 61.02	4.56 4.53	13.44 13.73	
2b$_3$	$C_{30}H_{44}BN_7O_3Zn \cdot H_2O$ 626.92 + 18.01		55.87 56.20	7.19 7.04	15.20 15.38	
3a	$C_{46}H_{52}BN_7O_3Zn$ 827.16		66.80 64.96	6.34 6.19	11.85 11.37	7.91 8.03
3b$_1$	$C_{46}H_{48}BF_5N_6OZn$ 872.12		63.35 62.68	5.55 5.50	9.64 9.49	7.50 7.41
3b$_2$	$C_{31}H_{42}BF_5N_6OZn \cdot CH_2Cl_2$ 685.90 + 84.93		49.86 50.15	5.75 5.85	10.90 10.64	8.48 8.58
4a	$C_{41}H_{48}BF_3N_6OZn$ 774.06		63.62 63.04	6.25 6.26	10.86 10.89	8.45 8.51
4b	$C_{41}H_{48}BCl_3N_6OZn \cdot \frac{1}{2}C_6H_6$ 823.43 + 39.06		61.27 61.50	5.96 5.91	9.74 9.80	
5	$C_{41}H_{51}BN_6OSZn$ 752.16		65.47 64.92	6.83 6.74	11.17 11.20	

2b$_3$ (Nitr = nitrophenyl): δ = 1.35 [s, 27H, *t*Bu(pz)], 2.41 [s, 9H, Me(pz)], 5.87 [s, 3H, H(pz)], 6.84 [d, ^3J = 9.3 Hz, 2H, Nitr(2,6)], 8.12 [d, ^3J = 9.3 Hz, 2H, Nitr(3,5)].

2c: δ = 1.17 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 1.99 [s, 3H, Me(phenolate)], 2.48 [s, 9H, Me(pz)], 2.73 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 5.41 [d, ^3J = 7.8 Hz, 1H, phenolate H5], 5.93 [t, ^3J = 7.8 Hz, 1H, phenolate H4], 6.12 [s, 3H, H(pz)], 6.86 [d, 6H, Phe(3,5)], 7.08 [d, ^3J = 7.8 Hz, 1H, phenolate H3], 7.42 [d, ^3J = 7.8 Hz, 6H, Phe(2,6)].

2d (Sal = 2-Hydroxybenzyl): δ = 1.16 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.48 [s, 9H, Me(pz)], 2.66 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 4.47 [s, 1H, CH_2OH(Sal)], 4.50 [s, 1H, CH_2OH(Sal)], 5.08 [d, ^3J = 7.8 Hz, 1H, Sal H6], 5.77 [t, ^3J = 7.8 Hz, 1H, Sal H5], 5.86 [t, ^3J = 7.8 Hz, 1H, Sal H4], 6.15 [s, 3H, H(pz)], 6.54 [d, ^3J = 7.8 Hz, 1H, Sal H3], 6.94 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.46 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)]. **2e**: δ = 1.16 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 1.92 [s, 3H, Me(phenolate)], 2.49 [s, 9H, Me(pz)], 2.72 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 3.36 [s, 1H, CH_2OH(phenolate)], 3.42 [s, 1H, CH_2OH(phenolate)], 3.55 [s, 1H, CH_2OH(phenolate)], 3.57 [s, 1H, CH_2OH(phenolate)], 6.12 [s, 3H, H(pz)], 7.09 [m, 2H, phenolate H3)], 7.09 [m, 6H, Phe(3,5)], 7.54 [d, 6H, Phe(2,6)].

3a (Nitr = nitrophenyl): δ = 1.17 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.50 [s, 9H, Me(pz)], 2.85 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 4.62 [s, 2H, CH_2O], 6.18 [s, 3H, H(pz)], 7.20 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.45 [d, ^3J = 8.8 Hz, 2H, Nitr(2,6)], 7.74 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)], 8.17 [d, ^3J = 8.8 Hz, 2H, Nitr(3,5)].

3b$_1$: δ = 1.23 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.52 [s, 9H, Me(pz)], 2.89 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 4.63 [s, 2H, CH_2O], 6.22 [s, 3H, H(pz)], 7.27 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.77 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)].

3b$_2$: δ = 1.29 [s, 27H, *t*Bu(pz)], 2.31 [s, 9H, Me(pz)], 4.73 [s, 2H, CH_2O], 5.73 [s, 3H, H(pz)].

4a: δ = 1.16 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.43 [s, 9H, Me(pz)], 2.83 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 3.25 [q, ^3J(H,F) = 9.4 Hz, 2H, CH_2CF_3], 6.13 [s, 3H, H(pz)], 7.19 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.66 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)].

4b: δ = 1.24 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.55 [s, 9H, Me(pz)], 2.92 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 3.73 [s, 2H, CH_2CCl_3], 6.27 [s, 3H, H(pz)], 7.32 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.76 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)].

5: δ = 1.18 [t, ^3J = 6.0 Hz, 2H, SCH_2], 1.26 [d, ^3J = 6.9 Hz, 18H, Me(*i*Pr)], 2.54 [s, 9H, Me(pz)], 2.67 [t, ^3J = 6.0 Hz, 2H, OCH_2], 2.93 [sept, ^3J = 6.9 Hz, 3H, H(*i*Pr)], 6.15 [s, 3H, H(pz)], 7.28 [d, ^3J = 8.2 Hz, 6H, Phe(3,5)], 7.62 [d, ^3J = 8.2 Hz, 6H, Phe(2,6)].

Structure Determinations[26]: All crystals were taken directly from the reaction products. The data sets were obtained with a Nonius CAD4 diffractometer by the ω/2Θ technique using graphite-filtered Mo-K_α radiation. An absorption correction based on azimutal scans was applied to **2b$_1$**. The structures were solved with direct methods and refinced anisotropically. H atoms were included with C–H = 0.96 Å and isotropic temperature factors 1.2 times those

Table 4. Crystallographic details

	2b$_1$	**3b$_1$**	**4a**	**4b**	**5**
cystal size (mm)	0.7·0.7·0.6	0.5·0.5·0.2	0.5·0.5·0.2	0.5·0.5·0.5	0.8·0.6·0.6
cystal system	monoclinic	monoclinic	monoclinic	trigonal	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-3	P-1
Z	4	4	4	2	2
a(Å)	14.618(1)	9.7898(4)	13.091(3)	14.260(1)	12.115(2)
b(Å)	14.130(1)	20.086(2)	18.047(4)	14.260(1)	13.775(3)
c(Å)	22.220(1)	20.436(7)	17.891(4)	12.759(1)	14.242(3)
α(°)	90	90	90	90	74.73(3)
β(°)	97.52(4)	96.034(3)	99.09(3)	90	68.04(3)
γ(°)	90	90	90	120	83.45(3)
V(Å^3)	4550.1(5)	3996.3(4)	4173.7(16)	2246.9(3)	2126.2(7)
$d_{calcd.}$ (g cm^{-3})	1.24	1.45	1.23	1.25	1.22
$d_{obsd.}$ (g cm^{-3})	1.23	1.41	1.18	1.25	1.21
μ(mm^{-1})	0.59	0.68	0.64	0.76	0.67
Θ range	2.3-26.3	2.6-28.7	4.3-22.5	2.9-26.3	2.4-26.0
refl. measd.	9590	8820	5675	1783	8800
indep.refl.obsd.[I>2σ(I)]	5868	5916	2681	1369	5146
parameters	580	541	448	184	478
R(obsd.refl.)	0.043	0.050	0.084	0.063	0.057
wR2(all refl.)	0.142	0.167	0.285	0.218	0.186
res.el.density (e/Å^3)	+0.3 -0.3	+0.7 -0.4	+0.6 -0.6	+0.5 -0.4	+0.7 -0.3

of their attached atoms (1.5 times in methyl groups). The computer programs by Sheldrick[27] and Keller[28] were used. The crystallographic details are listed in Table 4.

☆ Dedicated to Professor *Wolfgang Beck* on the occasion of his 65th birthday.

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