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Pyrazolylborate–Zinc Alkoxide Complexes. 3. Acid–Base Reactions

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The alkoxides $Tp^{Ph,Me}$Zn–OR (R = Me, Et, i-Pr) undergo acid–base reactions with all hydrogen compounds whose acidity is higher than that of the corresponding alcohol ROH. Thus, anion exchange occurs with the common acids acetic acid, acetohydroxamic acid, acetylacetone, phenol, and ethylmercaptan. Alkoxide exchange is observed using methanol, ethanol, and trifluoroethanol. With the NH acids cyanamide, trifluoroacetamide, and pyrazoles, the corresponding anions are attached to zinc, and likewise β- and γ-lactams, a thiazolidinedione, and the cyclic sulfimide saccharin are deprotonated. Of the CH acids acetonitrile forms the Tp*Zn–cyanomethanide. Acetone is deprotonated by the cyanomethanide complex and incorporated as the Tp*Zn–β-ketoiminate.

Introduction

In the preceding papers of this series,[1,2] we described two of the three basic properties of alkoxide ligands in pyrazolylborate−zinc alkoxide complexes, namely their high nucleophilicity and their pronounced leaving-group quality. This paper deals with the third property, their lability toward even very weak Brønsted acids.

We had observed early on[3−7] that the hydroxide ligand in pyrazolylborate−zinc hydroxide complexes can be replaced by the anions of common acids upon reaction with the HX compounds, including phenols, fluorinated alcohols, acetylacetone, or H_2S. These reactions can be described as acid−base reactions, requiring that the acidity of the reagent HX is higher than that of H_2O. Mechanistically they can be looked at as a protonation of the zinc-bound OH^-, converting it to the uncharged and labile H_2O, which is then replaced by X^-.

In line with this it was observed by Parkin that the reactions of the hydroxide complexes with alcohols lead to equilibrium mixtures containing only very small amounts of the alkoxide complexes.[8] The equilibrium constants depend characteristically on the pK_a values of the alcohols but also on relative bond strengths.[9] Furthermore, hydrogen-bonding interactions can greatly stabilize the zinc alkoxide combination,[10,11] which makes it understandable that in an enzymatic environment like that of alcoholdehydrogenase[12] a zinc ethoxide function can persist even in the presence of water.

Simple pyrazolylborate−zinc alkoxide complexes, however, are so sensitive toward hydrolylsis that glovebox techniques are essential for their handling.[1,8] Assuming that their behavior toward HX species would correspond mechanistically to that of the hydroxide complexes, one could therefore expect reactions of the alkoxides with HX compounds of all kinds. These should include reactions with very weak Brønsted acids leading to new types of pyrazolylborate−Zn−X complexes.

This paper reports such reactions. Common weak acids were used to verify the proteolytic lability of the Zn−OR function. Alcohols were used to test the acid−base considerations. A wide range of NH-containing compounds was found suitable for proteolysis, and even acetonitrile and acetone underwent CH deprotonations. The reactions were performed with the alkoxides **1a**−**c**.

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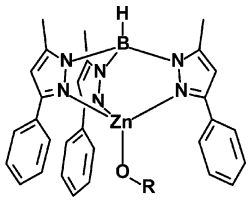

$Tp^{Ph,Me}Zn-OR$

1a: R = CH_3, **1b**: R = C_2H_5, **1c**: R = $CH(CH_3)_2$

Results and Discussion

Common Acids. The extreme water sensitivity of the complexes **1** allowed the conclusion that they would be hydrolyzed with the same ease by weak acids. This was verified using acetic acid, ethanethiol, and phenol. Reactions according to eq 1 produced the known acetate **2**,[13] ethanethiolate **3**,[14] and phenolate **4**[5] in very good yields. Likewise, aliphatic OH compounds of sufficient acidity effected the replacement of the alkoxide group from **1a**. 2,2,2-Trifluoroethanol yielded the fluoroalkoxide **5**[5] and acetylacetone yielded the chelate complex **6**. Finally, acetohydroxamic acid afforded the known chelate complex **7**.[15]

$$\underset{\mathbf{1a}}{Tp^{Ph,Me}Zn-OMe} + HX \rightarrow \underset{\mathbf{2-7}}{Tp^{Ph,Me}Zn-X} + HOMe$$

no.	**2**	**3**	**4**	**5**	**6**	**7**
X	CH_3COO	C_2H_5S	C_6H_5O	CF_3CH_2O	acetyl acetonate	aceto-hydroxamate

The reaction between **1a** and 2,2,2-trifluoroethanol is an alkoxide exchange, i.e., the more acidic alcohol releases the less acidic one. Such exchange reactions could also be performed with purely aliphatic alcohols. Thus the isopropoxide **1c** was converted to the ethoxide **1b** by reaction with ethanol, and the latter in turn was converted to the methoxide **1a** by reaction with methanol.

The known complexes **2**−**5** and **7** were identified by their NMR spectra. The new acetylacetonate **6** was subjected to a structure determination, the main purpose of which was the comparison with the β-ketoiminate complex **17** (see below). Figure 1 shows the structure of **6**. The Zn−O bond lengths and the shape and orientation of the acac ligand correspond to those in other Tp*Zn−β-ketoenolates.[4,16] The ZnO_2C_3 chelate ring is virtually planar, and N1 and O2 occupy the axial positions in the distorted trigonal bipyramidal coordination environment of zinc.

NH Compounds. A wide range of acidic NH compounds was subjected to reactions with **1a**, and many more can be conceived. These reactions have opened the way to Tp*Zn−X complexes, with X being an anionic nitrogen ligand derived from an NH compound of low acidity, a class of compounds which had not been accessible starting from Tp*Zn−OH or Tp*Zn−Cl before.

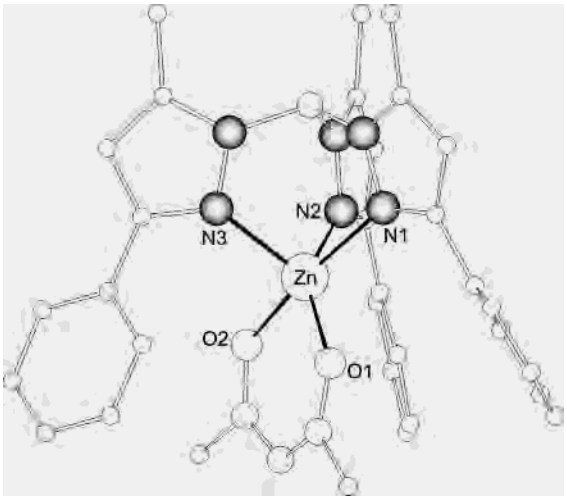

Figure 1. Molecular structure of $Tp^{Ph,Me}Zn(acac)$ (**6**). Relevant bond lengths (Å) and angles (deg): Zn−N1, 2.168(5); Zn−N2, 2.098(4); Zn−N3, 2.045(5); Zn−O1, 1.952(4); Zn−O2, 2.024(4); O1−Zn−O2, 90.0(2); N1−Zn−O2, 170.8(2).

The simplest NH acid used was cyanamide. Originally cyanamide had been hoped to react as the heterocumulene diimide and be inserted as such in the Zn−OR bond.[1] Its reaction as a NH acid made us aware of the potential of such reactions. The cyanoimide complex **8** resulted in very good yields from **1a** and H_2NCN. It is characterized by a ν(CN) IR band at 2183 cm^{-1} and a NH proton NMR resonance in $CDCl_3$ at 4.25 ppm. As crystals of **8** suitable for a structure determination could not be obtained, its structural assignment must rest on the spectroscopic relation with the few other metal−cyanoimide complexes.[17−19]

$$\underset{\mathbf{8}}{Tp^{Ph,Me}Zn-NH-CN} \quad \underset{\mathbf{9}}{Tp^{Ph-Me}Zn-NH-COCF_3}$$

Simple amides such as acetamide were not acidic enough to react with complexes **1**. But trifluoroacetamide and **1c** proved to be a sufficiently reactive combination to yield the solvolysis product **9**. Complex **9** is characterized by its ν(CO) IR band at 1686 cm^{-1}, which is slightly lower than the band of the related trifluoroacetate complex.[13] Its NH proton gives rise to a NMR signal at 4.73 ppm in $CDCl_3$, and the ^{19}F resonance of the CF_3 group occurs at −75.5 ppm. Again crystals of **9** for a structure determination could not be obtained.

Since Tp*Zn−pyrazolide complexes had already been obtained as decomposition products of their pyrazolylborate ligands,[16,20] one could anticipate that pyrazoles would be sufficiently strong acids to cleave the alkoxide complexes and be incorporated as pyrazolide ligands. This was borne out by the reactions of **1a** with pyrazole and of **1b** with 3-phenyl-5-methylpyrazole (the constituent of the pyrazolylborate ligand in complexes **1**). While the first reaction

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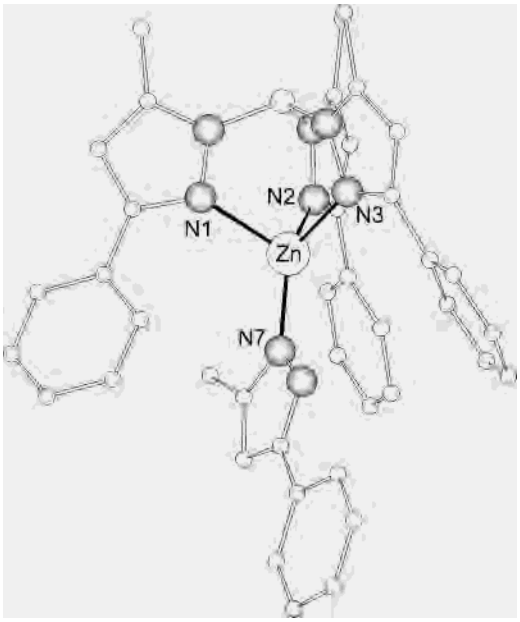

Figure 2. Molecular structure of complex **11**. Relevant bond lenths (Å): Zn−N1, 2.033(7); Zn−N2, 2.069(7); Zn−N3, 2.012(7); Zn−N7, 1.897(6).

resulted in a product mixture containing **10** among other complexes, the second was clean and essentially quantitative, resulting in crystalline **11**. The identities of **10** and **11** are evidenced by the characteristic high-field shifts of the pyrazolides' ^{1}H NMR signals, which result from the embedding of the pyrazolides between the phenyl rings of the $Tp^{Ph,Me}$ ligands.

$Tp^{Ph,Me}Zn-$pyrazolide
10
$Tp^{Ph,Me}Zn-$3-phenyl-5-methylpyrazolide
11

Complex **11** was subjected to a structure determination, which is the first one of a Tp*Zn−pyrazolide complex. As Figure 2 shows, the pyrazole ring is sandwiched between two phenyl rings. The only bond length worth mentioning is that of the Zn−N(pyrazolide) bond, 1.90 Å. It is more than 0.1 Å shorter that the other Zn−N bonds in **11**, representing the anionic nature of the pyrazolide. The only other Tp*Zn−X complex with a monodentate uncharged nitrogen ligand X that was structurally characterized is $[Tp^{Cum,Me}Zn-$pyridine$]ClO_4$.[21] Its Zn−N bond to the pyridine ligand is 1.97 Å long.

When we reacted lactams with **1a**, we initially expected ring-opening reactions related to the hydrolytic cleavage of a β-lactam by $Tp^{Cum,Me}Zn-OH$.[13] Hence their deprotonations came as a surprise to us. Both β-propiolactam with $Tp^{Cum,Me}Zn-OMe$[1] and γ-butyrolactam with **1a** yielded the amide complexes **12** and **13**. The characteristic features in the spectra of **12** and **13** are their ν(CO) IR bands at 1709 and 1692 cm^{-1}, respectively, and the high-field shifts of all lactam ^{1}H NMR signals by about 1 ppm, due to the proximity of all lactam H atoms to the Tp* ligands' phenyl groups.

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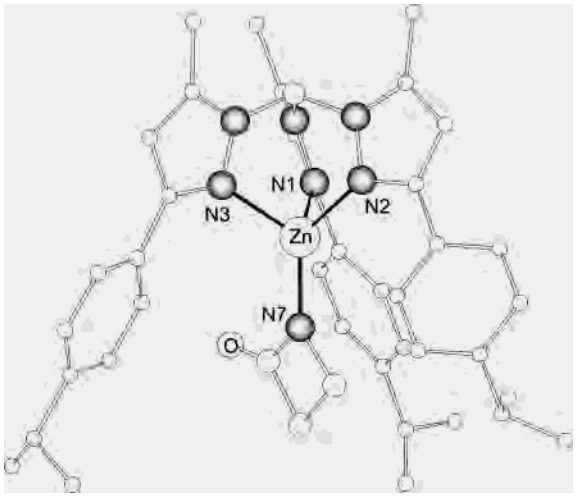
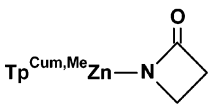


Figure 3. Molecular structure of one of the two independent molecules of complex **12**. Relevant bond lengths (Å): Zn−N1, 2.059 and 2.041(2); Zn−N2, 2.063 and 2.064(2); Zn−N3, 2.050 and 2.050(2); Zn−N7, 1.898 and 1.889(3).



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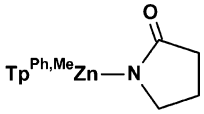
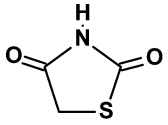


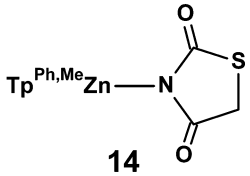
13

The structure determination of **12** (see Figure 3) confirmed the assignments. Like in **11** the Zn−N7 bond (1.90 Å) is much shorter than the other Zn−N bonds. The five atoms of the lactamide and the zinc ion are coplanar within ±0.05 Å. We did not find another zinc−lactamide complex in the literature, but there are a few such complexes of other metals.[22−24]

We included two sulfur-containing heterocycles with NH functions in the investigation. Of these, 2,4-thiazolidinedione is bifunctional, being a cyclic amide as well as a cyclic thioester. It was to be tested whether the high thiophilicity of zinc would lead to ring opening at the S−CO bond, as previously observed upon reaction of **1a** with γ-thiobutyrolactone,[2] or whether the enhanced acidity of the NH function between the two carbonyl groups would lead to a preference for NH deprotonation. The latter was the case. Reaction with **1a** produced a high yield of complex **14**.



thiazolidine-dione



14

Complex **14** gives rise to a single ν(CO) band in the IR at 1644 cm^{-1} and a single proton NMR resonance at 2.96 ppm in $CDCl_3$. The structure determination of **14** (see Figure 4) verified the attachment of the thiazolidinedionate to zinc as

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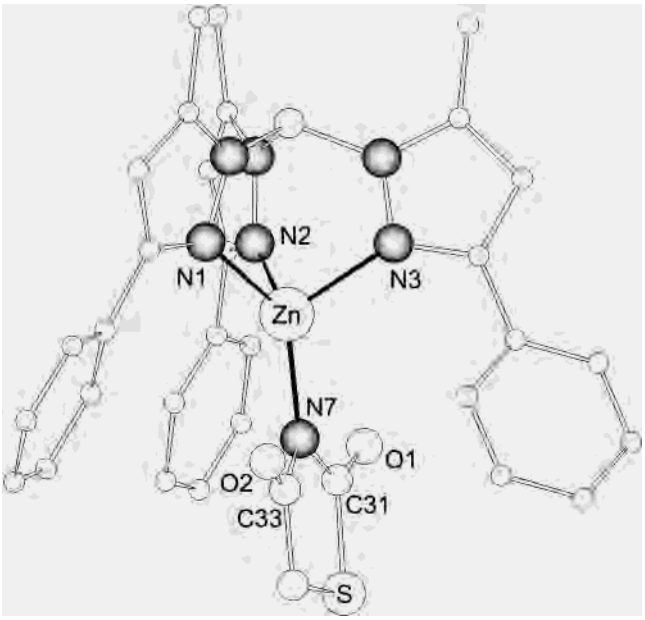


Figure 4. Molecular structure of complex **14**. Relevant bond lengths (Å): Zn−N1, 2.046(2); Zn−N2, 2.040(2); Zn−N3, 2.043(2); Zn−N7, 1.940(2); N7−C31, 1.370(3); N7−C33, 1.365(3).

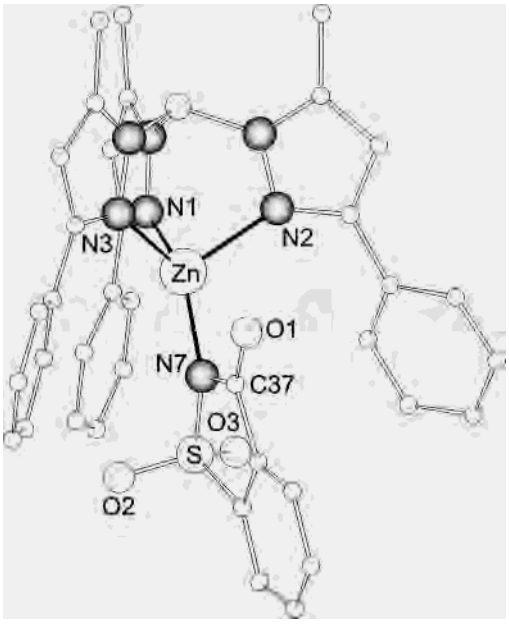
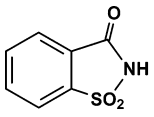


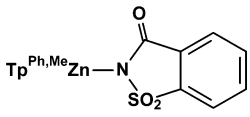
Figure 5. Molecular structure of complex **15**. Relevant bond lengths (Å): Zn−N1, 2.032(5); Zn−N2, 2.040(5); Zn−N3, 2.010(5); Zn−N7, 1.958(5); N7−S, 1.637(5); N7−C37, 1.383(7).

a rather symmetrical diacylamide. The Zn−N7 bond (1.94 Å) is slightly longer than those in **11** and **12**. It corresponds to that in the structurally related 1-methyluracilate complex (1.93 Å),[25] while the structurally related dihydrouracilate[26] and theobrominate complexes[25] both show Zn−N bond lengths of 1.90 Å. Like **14**, the latter complexes are derived from rather acidic diacylamines and are therefore accessible by reactions of the nucleobases with Tp*Zn−OH.

The cyclic amide *o*-benzoic acid sulfimide (saccharin) is also a rather strong acid that in addition contains two hydrolyzable N−X bonds. Yet, like before with the thiazolinedione, complex **1a** did not induce ring opening. Deprotonation with formation of complex **15** was the preferred reaction.



saccharin



15

The IR spectrum of **15** shows the ν(CO) band at 1698 cm^{-1} and ν(SO) bands at 1172 and 1153 cm^{-1}. There are no characteristic ^{1}H NMR resonances of **15**, which therefore had to be identified by a structure determination (see Figure 5). Complex **15** shows the most severe deviation of the Zn−N7 axis from the Tp ligand's 3-fold axis Zn−B (16.5°) and the longest Zn−N7 bond (1.96 Å) of the Zn−N complexes described here. There are two related zinc−saccharinate complexes in the literature[27,28] whose Zn−N bond lengths (1.97 and 1.98 Å) are very similar to that in **15**.

CH Acids. Compared to the pK_a values of methanol (15.5), ethanol (15.9), and 2-propanol (17.0),[29] those of acetonitrile (25)[30] and acetone (20)[31] are so high that one would not expect a release of the alcohols from complexes **1** by reaction with them, corresponding to the fact that acetonitrile is a suitable solvent for the hydrides Tp*Zn−H. This seemed to be confirmed by the inertness of acetonitrile toward **1a**. But upon dissolution of **1b** in acetonitrile an uncontrolled decomposition set in, and in acetonitrile the isopropoxide **1c** was cleanly converted to the cyanomethanide **16**. This demonstrates that the relative acidities of the alcohols and the reagents can be only a rough guideline for predicting the solvolytic reactions.

$$Tp^{Ph,Me}Zn-CH_2CN$$

16

Complex **16** is characterized by a ν(CN) IR band at 2260 cm^{-1} and a ^{1}H NMR resonance for the methylene group at 0.27 ppm. Its pleasantly simple molecular structure is shown in Figure 6. The cyanomethanide ligand contains a strictly linear CCN unit and has a bending angle of 117° at the methylene group. The Zn−C bond length of 1.99 Å corresponds to those in $Tp^{tBu}Zn-CH_3$[32] and $Tp^{Me,Me}Zn-CH_3$.[33] While cyanomethanide complexes are not uncommon in organometallic chemistry, **16** seems to be the first such complex of zinc.

Having found that acetonitrile is able to protonate the alkoxide ligands of **1b** and **1c**, we anticipated that acetone would do so too. Yet reactions of **1a**−**c** with acetone were

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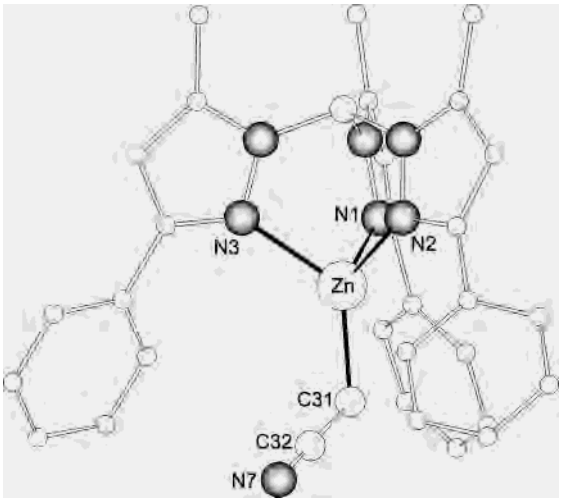


Figure 6. Molecular structure of complex **16**. Relevant bond lengths (Å) and angles (deg): Zn−N1, 2.072(5); Zn−N2, 2.069(4); Zn−N3, 2.074(4); Zn−C31, 1.991(6); C31−C32, 1.43(1); C32−N7, 1.14(1); Zn−C31−C32, 116.6(5); C31−C32−N7, 179(1).

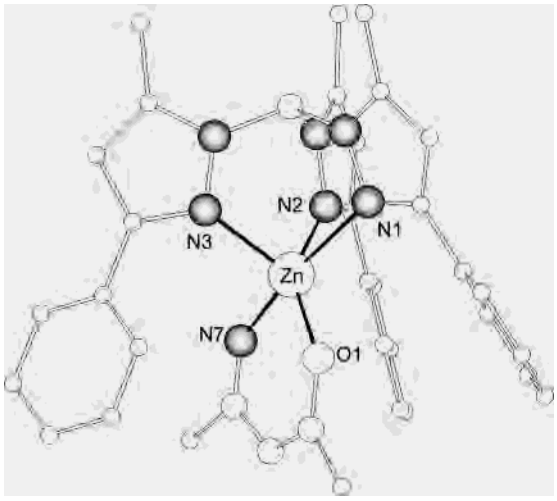
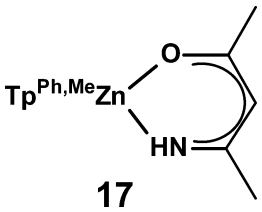


Figure 7. Molecular structure of complex **17** (one of the two disordered molecules). Relevant bond lengths (Å) and angles (deg): Zn−N1, 2.282(5); Zn−N2, 2.056(6); Zn−N3, 2.084(5); Zn−O1, 1.94 or 1.98(2); Zn−N7, 2.02 or 1.98(2); N1−Zn−N7, 168.3 or 174.4(5).

inconclusive, leading to $Tp^{Ph,Me}Zn-OH$ as the only isolated product. This may have to do with the fact that acetone can hardly be completely dehydrated without subjecting it to partial decomposition.

We then tried to use complex **16** as the species that is protonated by acetone with release of acetonitrile and attachment of the resulting enolate to zinc. To our surprise, this reaction led to the incorporation of acetone and formation of the β-ketoiminate complex **17**. This incorporation corresponds to a double deprotonation of acetone at one methyl group and protonations at both ends of the cyanomethanide ligand. The resulting iminopentanoate ligand must then be formed by C−C coupling resulting from nucleophilic attack of the enolate at the nitrile carbon.



17

Complex **17** was subjected to an extensive NMR analysis including the detection of the imino nitrogen by $^{1}H-^{15}N$-correlation methods. The resulting NMR data (see Experimental) are in agreement with the structure obtained by X-ray analysis (see Figure 7). The crystal data and the molecular shape of **17** are very similar to those of the acetylacetonate complex **6** (see above). Furthermore, there seems to be an orientational 1:1 disorder of the β-ketoiminate ligand leading to split postitions for its two zinc-bound atoms O and N. This prohibits a discussion of the zinc−ligand bond lengths, and it necessitated the detection of the NH group by NMR methods. Yet the trigonal bipyramidal coordination of the zinc ion with N1 and N7 in axial positions and the coplanarity of the six-membered chelate ring, just like in **6**, underline the isoelectronic nature of the acetylacetonate and β-ketoiminate ligands. While substituted β-ketoiminates are frequent members of the Schiff base class of ligands, the unsubstituted 4-iminopentan-2-oate is a rare species, existing in only one palladium complex[34] in the open literature.[35]

Conclusions

The leaving group properties of the alkoxide ligands in these complexes, which had already been exploited in the preceding papers,[1,2] are also the basis of the rich acid−base chemistry found here. While the pyrazolylborate−zinc derivatives of the reasonably acidic OH and NH compounds employed here are normally accessible from Tp*Zn−OH as well, the new entry to complexes such as **8**, **10**, **12**, and **16** underlines the value of the alkoxides in the area. Finally, the condensation reaction leading to **17**, which may involve a zinc−enolate intermediate, is a reminder that the organic chemistry of covalently bound zinc−enolates should be as rich as, but different from, that of the ionic enolates generated by strong bases.

This paper completes our series of investigations on pyrazolylborate−zinc alkoxide complexes. In all three fields of study, insertions into the Zn−O bonds,[1] solvolytic substrate cleavages,[2] and acid−base reactions, the Tp*Zn−OR species have been found to be versatile reagents. Thus, in our opinion, the inconveniences associated with their synthesis are more than compensated by their rich chemistry.

Experimental Section

General Data. All experimental techniques and the standard IR and NMR equipment were as described previously.[36] The Tp*Zn−alkoxides were prepared as described.[1] Organic reagents were purchased from Merck and Aldrich. All manipulations involving the Tp*Zn−alkoxide complexes were performed in a Braun

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Labmaster 130 glovebox with degassed and dried solvents. 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 in comparison to the reference compounds.[1,3,5,14] 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.

Reactions with Common Acids. The reagents **1a**, acetic acid, ethylmercaptan, phenol, 2,2,2-trifluoroethanol, and acetohydroxamic acid were used as 0.01 M solutions in dichloromethane. Equimolar amounts of the reagents (10 mL each) were combined and the mixtures stirred overnight. Then all volatiles were removed in vacuo, the residues were dissolved in exactly 5 mL of $CDCl_3$ and subjected to ^{1}H NMR spectroscopy. From their signal intensities the yields of the known products were determined as 98% for **2**,[13] 75% for **3**,[14] 65% for **4**,[5] 95% for **5**,[5] and 87% for **7**.[15]

Complex 6. Acetylacetone (36 μL, 35 mg, 0.34 mmol) was added to a solution of 200 mg (0.34 mmol) of **1a** in 20 mL of toluene. After stirring at 50 °C for 16 h all volatiles were removed in vacuo. Recrystallization from hot acetonitrile yielded 209 mg (88%) of **6** as colorless crystals, mp 215 °C (dec). IR (KBr): 2539w (BH), 1600s (CO). ^{1}H NMR ($CDCl_3$): 1.04 (s, 6H, CH_3), 4.81 (s, 1H, CH). Anal. Calcd for $C_{35}H_{35}BN_6O_2Zn{\cdot}CH_3CN$ (M_r = 647.90 + 41.05): C, 64.50; H, 5.56; N, 14.23. Found: C, 63.64; H, 5.92; N, 14.02.

Alkoxide Exchange. 1b (48 mg, 0.08 mmol) in 10 mL of dichloromethane was treated with 2 mL (0.08 mmol) of a 0.04 M solution of methanol in dichlorometane. Likewise, 49 mg (0.08 mmol) of **1c** was treated with 0.08 mmol of ethanol. The solutions were stirred for 4 h. Then all volatiles were removed in vacuo and the residues dissolved in exactly 5 mL of $CDCl_3$ and subjected to ^{1}H NMR spectroscopy. From the intensities of their resonances the yields were determined as 90% of **1a** from **1b** and 93% of **1b** from **1c**.

Complex 8. Cyanamide (15 mg, 0.36 mmol) was added to a solution of 200 mg (0.34 mmol) of **1a** in 20 mL of toluene. After stirring at 50 °C for 16 h, all volatiles were removed in vacuo. Recrystallization from hot acetonitrile yielded 146 mg (72%) of **8** as a colorless powder, mp 174 °C. IR (KBr): 2547w (BH), 2183s (CN). ^{1}H NMR ($CDCl_3$): 4.25 (s, 1H, NH). Anal. Calcd for $C_{31}H_{29}BN_8Zn{\cdot}CH_3CN$ (M_r = 589.82 + 41.05): C, 62.83; H, 5.11; N, 19.98. Found: C, 62.87; H, 5.07; N, 21.06.

Complex 9. Trifluoroacetamide (37 mg, 0.33 mmol) was added to a solution of 200 mg (0.33 mmol) of **1c** in 10 mL of toluene. After stirring at 50 °C for 5 h, all volatiles were removed in vacuo. Recrystallization from hot acetonitrile yielded 141 mg (65%) of **9** as a colorless powder, mp 229 °C. IR (KBr): 2458w (BH), 1686s (CO). ^{1}H NMR ($CDCl_3$): 4.73 (s, 1H, NH). ^{19}F NMR ($CDCl_3$): −75.5. Anal. Calcd for $C_{32}H_{29}BF_3N_7OZn$ (M_r = 660.82): C, 58.16; H, 4.42; N, 14.84. Found: C, 58.52; H, 4.73; N, 15.21.

Complex 10. Pyrazole (23 mg, 0.34 mmol) was added to a solution of 200 mg (0.34 mmol) of **1a** in 15 mL of benzene. After stirring for 18 h, all volatiles were removed in vacuo, and the residue was crystallized from dichloromethane/acetonitrile. Then, 141 mg of a colorless powder remained, the ^{1}H NMR spectrum of which showed that it contained more than one product. In this mixture complex **10** was identified by its pyrazole ^{1}H NMR resonances in $CDCl_3$ at 6.10 (s) and 7.35 ppm (m), which were of similar intensity as the pyrazole resonances of the coproducts.

Complex 11. 3-Phenyl-5-methylpyrazole (40 mg, 0.25 mmol) was added to a solution of 150 mg (0.25 mmol) of **1b** in 20 mL of toluene. After stirring for 24 h, all volatiles were removed in vacuo. Recrystallization from acetone by layering with *n*-heptane yielded 112 mg (63%) of **11** as colorless crystals, mp 260 °C (dec). IR (KBr): 2535m (BH). ^{1}H NMR ($CDCl_3$): 0.98 (s, 3H, Me), 5.77 (s, 1H, pz-H), phenyl resonances among the phenyl multiplets of the $Tp^{Ph,Me}$ ligand. Anal. Calcd for $C_{40}H_{37}BN_8Zn$ (M_r = 705.99): C, 68.05; H, 5.28; N, 15.87; Found: C, 67.06; H, 5.27; N, 15.70.

Complex 12. β-Propiolactam (21 mg, 0.30 mmol) was added to a solution of 200 mg (0.28 mmol) of $Tp^{Cum,Me}Zn-OMe$[1] in 20 mL of benzene. After stirring at 50 °C for 18 h, all volatiles were removed in vacuo. Recrystallization from acetone/ethanol yielded 171 mg (81%) of **12** as colorless crystals, mp 258 °C (dec). IR (KBr): 2525w (BH), 1709s (CO). ^{1}H NMR ($CDCl_3$): 1.72 (t, J = 8.2 Hz, 2H, NCH_2), 2.27 (t, J = 8.2 Hz, 2H, CCH_2). Anal. Calcd for $C_{42}H_{50}BN_7OZn$ (M_r = 745.10): C, 67.70; H, 6.76; N, 13.16. Found: C, 66.80; H, 6.54; N, 12.77.

Complex 13. 2-Pyrrolidone (γ-butyrolactam) (18 μL, 20 mg, 0.25 mmol) was added to a solution of 143 mg (0.25 mmol) of **1a** in 15 mL of toluene. After stirring at 50 °C for 24 h, all volatiles were removed in vacuo. Recrystallization from hot acetonitrile yielded 136 mg (86%) of **13** as a colorless powder, mp 215 °C. IR (KBr): 2540w (BH), 1692s (CO). ^{1}H NMR ($CDCl_3$): 1.42 (m, 2H, β-CH_2), 1.44 (t, J = 6.0 Hz, 2H, γ-CH_2), 2.18 (t, J = 6.2 Hz, 2H, α-CH_2). Anal. Calcd for $C_{34}H_{34}BN_7OZn{\cdot}CH_3CN$ (M_r = 632.89 + 41.05): C, 64.16; H, 5.53; N, 16.63. Found: C, 63.83; H, 5.61; N, 16.31.

Complex 14. 2,4-Thiazolidinedione (40 mg, 0.35 mmol) was added to a warm solution of 200 mg (0.35 mmol) of **1a** in 10 mL of toluene. After stirring at 50 °C for 18 h, all volatiles were removed in vacuo. Recrystallization from hot acetonitrile yielded 195 mg (85%) of **14** as colorless crystals, mp 243 °C (dec). IR (KBr): 2546w (BH), 1644s (CO). ^{1}H NMR ($CDCl_3$): 2.96 (s, 2H, SCH_2). Anal. Calcd for $C_{33}H_{30}BN_7O_2SZn{\cdot}CH_3CN$ (M_r = 664.91 + 41.05): C, 59.55; H, 4.71; N, 15.87; S, 4.53. Found: C, 59.48; H, 4.92; N, 15.76; S, 3.81.

Complex 15. Saccharin (63 mg, 0.34 mmol) was added to a solution of 200 mg (0.34 mmol) of **1a** in 20 mL of toluene. After stirring for 4 h, all volatiles were removed in vacuo. Recrystallization from methanol/dichloromethane yielded 239 mg (91%) of **15** as colorless crystals, mp 240 °C (dec). IR (KBr): 2547w (BH), 1698s (CO). ^{1}H NMR ($CDCl_3$): 6.97 (t, J = 7.4 Hz, 2H, C_6H_4), 7.52 (m, 8H, Tp-Ph and C_6H_4). Anal. Calcd for $C_{37}H_{32}BN_7O_3SZn{\cdot}CH_3OH$ (M_r = 730.97 + 32.04): C, 59.82; H, 4.76; N, 12.85; S, 4.20. Found: C, 59.48; H, 4.96; N, 12.79; S, 4.13.

Complex 16. A solution of 200 mg (0.33 mmol) of **1c** in 30 mL of acetonitrile was stirred at 50 °C for 1 h. The volume of the solution was reduced to 15 mL in vacuo. Cooling to −20 °C yielded 143 mg (74%) of **16** as colorless crystals, mp 232 °C. IR (KBr): 2541m (BH), 2204m (CN). ^{1}H NMR ($CDCl_3$): 0.27 (s, 2H, CH_2). Anal. Calcd for $C_{32}H_{30}BN_7Zn$ (M_r = 588.84): C, 65.27; H, 5.14; N, 16.65. Found: C, 64.71; H, 5.41; N, 16.47.

Complex 17. 16 (150 mg, 0.25 mmol) was suspended in 20 mL of warm acetonitrile and 3 mL of acetone was added. After stirring at 50 °C for 24 h the volume of the solution was reduced in vacuo until precipitation set in. The solution was then filtered hot and cooled to 0 °C. Then, 114 mg (69%) of **17** was precipitated as colorless crystals, mp 204 °C (dec). IR (KBr): 3353m (NH), 2542w (BH), 1586s (CO). ^{1}H NMR ($CDCl_3$): 0.75 (s, 3H, CH_3CN), 1.46 (s, 3H, CH_3CO), 4.33 (s, 1H, CH), 5.41 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): 26.3 (CH_3CN), 27.6 (CH_3CO), 93.8 (CH), 172.7 (CN), 186.6 (CO). ^{15}N NMR ($CDCl_3$): The ^{15}N NMR shifts were acquired

Table 1. Crystallographic Data

	6	**11**	**12**	**14**	**15**	**16**	**17**
formula	$C_{35}H_{35}BN_6O_2Zn\cdot CH_3CN$	$C_{40}H_{37}BN_8Zn$	$C_{42}H_{50}BN_7OZn\cdot 0.5CH_3CN$	$C_{33}H_{30}BN_7O_2SZn\cdot CH_3CN$	$C_{37}H_{32}BN_7O_3SZn\cdot CH_3CN$	$C_{32}H_{30}BN_7Zn\cdot CH_3CN$	$C_{35}H_{36}BN_7OZn\cdot CH_3CN$
MW	688.95	705.99	765.61	705.96	772.02	629.89	687.97
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	4	2	4	2	2	4	4
a (Å)	17.206(2)	11.724(1)	25.014(2)	12.048(1)	11.682(1)	12.487(1)	16.631(13)
b (Å)	12.752(1)	12.339(1)	12.260(1)	12.501(1)	12.234(1)	25.565(3)	12.969(11)
c (Å)	16.514(2)	13.708(1)	28.007(3)	14.496(1)	13.296(1)	10.860(1)	16.544(13)
α (deg)	90	79.083(2)	90	65.780(1)	92.358(2)	90	90
β (deg)	93.275(2)	75.370(2)	107.886(2)	69.350(1)	106.553(2)	114.720(2)	95.023(13)
γ (deg)	90	71.174(2)	90	62.037(1)	92.744(2)	90	90
V (Å^3)	3617.3(6)	1803.5(3)	8174(1)	1723.5(2)	1816.5(3)	3149.2(6)	3555(5)
d_{calc} (g cm^{-3})	1.27	1.30	1.24	1.36	1.41	1.32	1.29
μ(Mo Kα) (mm^{-1})	0.72	0.72	0.64	0.82	0.78	0.82	0.73
R1 (obs refl)[a]	0.069	0.082	0.053	0.045	0.077	0.073	0.096
wR2 (all refl)[a]	0.246	0.298	0.176	0.123	0.249	0.261	0.252

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

by inverse detection {^{1}H−^{15}N} using a gradient-enhanced multiquantum coherence spectrum. The zinc-bound pyrazole nitrogens are assigned at −117.2, the boron-bound nitrogens at −151.3, and the β-ketoiminate nitrogen at −208.9 ppm vs CH_3NO_2. Anal. Calcd for $C_{35}H_{36}BN_7OZn\cdot CH_3CN$ (M_r = 646.92 + 41.05): C, 64.98; H, 5.61; N, 15.16. Found: C, 64.34; H, 5.96; N, 14.91.

Structure Determinations. All crystals for the X-ray measurements were obtained by recrystallization from acetonitrile. Diffration data were obtained at 210 K with a Bruker Smart CCD diffractometer and subjected to an empirical absorption correction. The structures were solved with SHELX.[37] Parameters were refined against F^2. Drawings were produced with SCHAKAL.[38] Table 1 lists the crystallographic data. The R values for complexes **11** and **17** are rather high, which in both cases results from disorder of one six-membered ring, as discussed in the text for **17**.

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

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