Pyrazolylborate−Zinc−Hydrosulfide Complexes and Their Reactions

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Four new hydrosulfide complexes Tp*Zn−SH of substituted pyrazolylborate ligands (Tp*) were prepared by reactions of Tp*Zn−OH with H_2S, and three of them were structurally characterized. Unlike the Tp*Zn−OH complexes they do not react with esters, phosphates, or CO_2, e.g. for thiolytic cleavage reactions. They also cannot be deprotonated, as various bases induce precipitation of ZnS and release of anionic Tp*. Acidic organic X−OH compounds (carboxylic acids, trinitrophenol, hexafluoroacetylacetone) replace the SH groups with formation of Tp*Zn−OX. Thiols undergo an entropy-driven SH substitution to yield the Tp*Zn−SR complexes. Like the Tp*Zn−SR complexes the Tp*Zn−SH complexes are quite reactive toward alkylation with methyl iodide, yielding Tp*Zn−I and CH_3SH. The kinetic investigation of the methylation of $Tp^{Ph,Me}$Zn−SH has shown it to be a clean second-order reaction, thereby indicating that the SH group is alkylated in the zinc-bound state.

Introduction

Compared to the ubiquity of water and hydroxide ligands, their congeners hydrogen sulfide and hydrosulfide are curiosities in coordination chemistry. Textbooks virtually ignore them, a comprehensive coverage[1] can list them on less than two pages, and only very recently has a comprehensive review on metal−hydrosulfide complexes appeared.[2] There is but a handful of H_2S complexes[1] and not much more than a dozen species L_nM−SH with a single terminal hydrosulfide ligand.[2−19] Their reactivity has been investigated only sparsely, and $(Ph_3P)_2Pt(H)$−SH,[4] $[(CO)_5W−SH]^-$,[10] and $(PMe_3)_2(CO)_3Re−SH$[19] are the only systems for which several reactions have been described.

The trivial reason for this is the thermodynamic stability and low solubility of the metal sulfides whose formation is always favored. This preference can only be outweighed by an increased inertness of the metal−hydrosulfide complexes, which in classical coordination chemistry is represented by the electronic configuration d^6 and d^8 for the heavy metals[3,4,8,13] and in organometallic chemistry by carbonyl complexes of the group 6 and 7 metals.[5,10,11,17−19] Modern coordination chemistry has added the use of encapsulating tripodal ligands for ensuring localized functionality and general inertness.[6,7,12,15,20]

Our own interest in metal−hydrosulfide complexes[17−19] arose from our old studies of metal carbonyls with functional sulfur ligands. It became revitalized for our zinc chemistry when we observed how easily the pyrazolylborate−zinc−hydrosulfide complexes are formed[20,21] and how stable they are. We therefore chose the group of hydrosulfide complexes Tp*Zn−SH of 3- and 5-substituted pyrazolylborate ligands (Tp*) for a comprehensive investigation of their reactivity. The Tp* ligands, which are known to encapsulate and protect the zinc ion,[22] were expected to ensure sufficient inertness, so that loss of zinc in the form of zinc sulfide should be avoided and all aspects of the functionality of the Zn−SH unit should be accessible.

Results and Discussion

Complexes Tp*Zn−SH. The high affinity between zinc and sulfur and the strong leaving tendency of the OH ligand in Tp*Zn−OH[22] make the formation of Tp*Zn−SH a straightforward process. Treatment of Tp*Zn−OH with H_2S[20] and even with CS_2[21] results in the replacement of the OH ligand by SH. We had applied the former reaction to prepare $Tp^{Cum,Me}$Zn−

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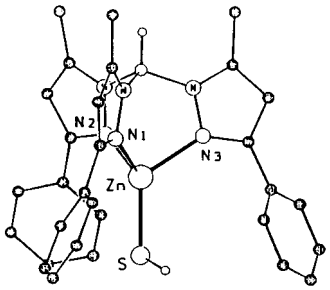

Figure 1. Molecular structure of **1a**.

Table 1. Bond Lengths (Å) and Angles (deg) in **1a**−**c**

	1a	**1b**	**1c**
Zn−N1	2.060(4)	2.05(2)	2.069(4)
Zn−N2	2.090(4)	2.04(2)	2.060(3)
Zn−N3	2.058(4)	2.04(2)	2.061(3)
Zn−S	2.219(2)	2.21(1)	2.214(1)
N1−Zn−S	123.5(1)	124.4(9)	121.2(1)
N2−Zn−S	124.0(1)	123.6(9)	123.6(1)
N3−Zn−S	123.6(1)	124.1(8)	125.8(1)

SH and the latter to obtain $Tp^{Ph,Me}Zn-SH$. Parkin et al.[15] had described yet another way to produce $Tp^{t-Bu}Zn-SH$ by reaction of $Tp^{t-Bu}Zn-H$ with H_2S. We now used the Tp*Zn−OH/H_2S reaction in dichloromethane to produce the hydrosulfide complexes **1a**−**d**.

$$Tp^{R,Me}Zn\text{-}SH$$

1a: R = phenyl, **1b**: R = 3-pyridyl, **1c**: R = 4-picolyl, **1d**: R = t-butyl

Complexes **1a**−**d** were obtained in high yields as colorless crystals which are stable up to at least 150 °C. Like other complexes of this class[15,20] they do not show a ν(SH) band in their IR spectra, but their NMR spectra in $CDCl_3$ solution show the SH resonance at −2 ppm for **1a**−**c** and at −1 ppm for **1d**. The additional high-field shift for **1a**−**c** is an expression of the embedding of the hydrosulfide ligand between the aromatic rings attached at the 3-positions of the pyrazole groups. NMR spectra taken in deuterated methanol show the SH resonances only in the beginning due to a slow SH/SD exchange.

The complete encapsulation of the SH ligands by the aromatic substituents is the main feature of the molecular structures of **1a**−**c**; see Figure 1 and Supporting Information. In all three cases the coordination of the zinc ions is trigonally distorted tetrahedral. The bonding details for all three complexes are quite similar, cf. Table 1, with practically identical Zn−S bond lengths and a very narrow spread of all Zn−N bond lengths and N−Zn−S angles.These bond lengths and angles are in the usual range observed for Tp*Zn−SX species.[20,23,24] It is noteworthy that the electronic "saturation" of the zinc ions by the hydrosulfide ligands causes a structural difference between **1b** or **1c** and their OH analogues $Tp^{Py,Me}Zn-OH$ or $Tp^{Pic,Me}Zn-OH$.[25] While **1b,c** are strictly four-coordinate, the latter are dimers in the solid state containing five-coordinate zinc due to the attachment of one pyridine nitrogen each from the opposing Tp*Zn−OH units.

Attempts at Nucleophilic Cleavages or Additions. The most prominent property of the Tp*Zn−OH complexes is the high nucleophilicity of their hydroxide ligands which enables them to perform hydrolytic cleavages of esters, amides, organophosphates, or oligophosphates and the hydration of CO_2.[22] It can be assumed that the hydrosulfide ligands in Tp*Zn−SH have at least the same nucleophilic strength and should enable similar cleavage reactions. We therefore treated complex **1a** with all the substrates that we had found to react with Tp*Zn−OH before.[22] No reaction took place, however, not even with the most reactive species such as trifluoromethyl acetate or tris(*p*-nitrophenyl)phosphate. Two explanations offer themselves to explain this failure. First the SH ligand is not nearly as good a leaving group as the OH ligand, due to the high affinity between zinc and sulfur. Second the Tp*Zn−SH complexes may not be suitable for the mechanism that we have proposed for the hydrolytic reactions of Tp*Zn−OH, which involves a four-center intermediate composed of the Zn−O unit and the E═O unit of the substrate.[22] As demonstrated above by the comparison of the $Tp^{Py,Me}Zn-OH$ and $Tp^{Py,Me}Zn-SH$ structures, the latter do not have the fendency to increase the coordination number of zinc by attachment of an additional nitrogen donor.

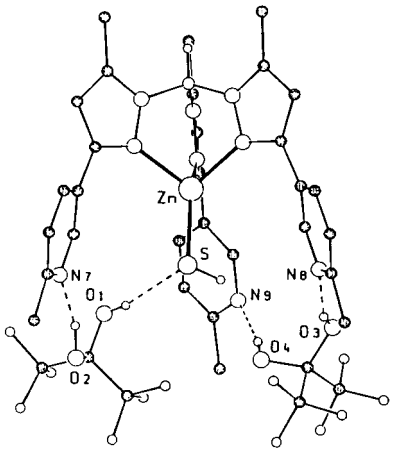

Figure 2. Structure of complex **2** (one of the two independent formula units).

In addition to the hydrolytic cleavages with Tp*Zn−OH we had also found its nucleophilic addition to electron-poor aldehydes with formation of α-hydroxyalkoxide complexes.[26] Such a reaction with Tp*Zn−SH would not require cleavage of the Zn−S bond, and hence, we tried it with the most reactive substrate trichloroacetaldehyde, yet again without any conversion. When **1c** was treated with hexafluoroacetone in wet dichloromethane/acetonitrile, complex **2** resulted in small yields. **2** is an unusual adduct between two molecules of hydrated hexafluoroacetone and one molecule of **1c**.

$$Tp^{Pic,Me}Zn\text{-}SH\bullet 2(CF_3)_2C(OH)_2$$
2

2 was not analytically pure but formed crystals which allowed its identification by a structure determination; see Figure 2. The asymmetric unit of the crystals contains two molecules of **2** which differ in orientational details but not in their hydrogen-bonding pattern. One hexafluoropropanediol molecule each is attached by O−H···N hydrogen bonds to two pyridine N atoms; the other is attached by one O−H···N interaction to the third pyridine nitrogen and by a O−H···S interaction to the sulfur. All OH and SH hydrogen atoms were located crystallographically. All hydrogen bonds are of intermediate strength (O−H···N = 2.66−2.76 Å, O−H···S = 3.11−3.18 Å; cf. Table 2). The $Tp^{Pic,Me}Zn-SH$ molecule itself does not change its bonding

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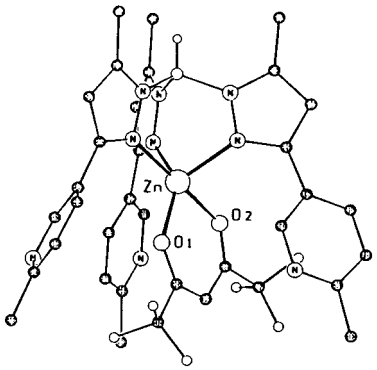

Figure 3. Molecular structure of **8b**. Bond lengths (Å): Zn−O1, 1.984(3); Zn−O2, 2.160(2); Zn−N1, 2.109(3); Zn−N2, 2.037(3); Zn−N3, 2.040(3).

Table 2. Selected Interatomic Distances (Å) in **2**

	molecule 1	molecule 2
Zn−N1	2.050(3)	2.053(3)
Zn−N2	2.054(3)	2.054(3)
Zn−N3	2.024(3)	2.027(3)
Zn−S	2.210(1)	2.203(1)
S···O1	3.114(4)	3.182(4)
O2···N7	2.665(4)	2.757(4)
O3···N8	2.709(4)	2.734(4)
O4···N9	2.678(4)	2.674(4)
S/O4	3.791(4)	3.498(4)

characteristics, its bond lengths and angles being very close to those in the free complex; cf. Tables 1 and 2. While the hydration of hexafluoroacetone is a common feature, we are not aware that a complex like **2** in which $(CF_3)_2C(OH)_2$ is attached in the secondary coordination sphere has been described.[27]

To increase the nucleophilic reactivity of the hydrosulfide complexes it was attempted to deprotonate them, aiming at hitherto unknown metallothiolates. However, as observed before for other hydrosulfide complexes,[10,19] this could not be achieved without destructive subsequent reactions. Both lithium methoxide and sodium methoxide induced the elimination of zinc sulfide upon reaction with $Tp^{Cum,Me}Zn-SH$, as did the organic base 1,5-diazabicyclo[4,3,0]no-5-ene (DBN) with $Tp^{Ph,Me}Zn-SH$. In all three cases the anionic pyrazolylborates remained as the corresponding salts **3a**−**c**, which were identified by their IR and NMR spectra.

$Li[Tp^{Cum,Me}]$ **3a** $Na[Tp^{Cum,Me}]$ **3b** $DBNH[Tp^{Ph,Me}]$ **3c**

When *n*-butyllithium was reacted with $Tp^{Cum,Me}Zn-SH$, SH substitution was observed instead of deprotonation, and the organozinc complex **4** was obtained, which extends the list of the rather stable Tp*Zn−R species.[23,28]

$Tp^{Cum,Me}Zn\text{-}C_4H_9$ **4**

Reactions with Acidic Organic Compounds. Whereas carboxylic functions could not be attached to the Tp*Zn units by thiolytic cleavage of esters with Tp*Zn−SH, they could be incorporated by acid−base reactions. Organic X−OH compounds which have a pK_a lower than 7 replace the SH ligand, forming Tp*Zn−OX and H_2S. While *p*-nitrophenol (pK_a = 7.15) did not react, trinitrophenol (picric acid, pK_a = 0.25) and $Tp^{Ph,Me}Zn-SH$ formed the picrate complex **5**. Likewise benzoic acid and phenylacetic acid yielded the carboxylates **6** and **7**. Hexafluoroacetylacetone was also acidic enough to undergo this reaction. With $Tp^{Ph,Me}Zn-SH$ (**1a**) and $Tp^{Pic,Me}Zn-SH$ (**1c**) it formed complexes **8a,b**.

$Tp^{Ph,Me}Zn\text{-}OC_6H_2(NO_2)_3$ **5**

$Tp^{Ph,Me}Zn\text{-}O\text{-}COPh$ **6**

$Tp^{Ph,Me}Zn\text{-}O\text{-}COCH_2Ph$ **7**

$Tp^{R,Me}Zn(hfa)$
8a: R = phenyl
8b: R = 4-picolyl

While the structures of **5**−**7** could be deduced with reference to similar complexes of this type,[23,29] those of **8a,b** left the ambiguity of mono- or bidentate coordination of the hfa ligands. The structure determination of **8b** (see Figure 3) revealed the chelating attachment, enforcing 5-fold coordination of zinc, as previously observed for Tp*Zn−cumoylacetonate[30] and acetylacetonate[31] complexes. The coordination geometry of zinc in **8b** is that of a distorted trigonal bipyramid with N1 and O2 on the axial positions and a N1−Zn−O2 angle of 174°. This causes an unsymmetrical attachment of both the pyrazolylborate and the acetylacetonate ligands with unusually long bonds for the axial and normal short bonds for the equatorial donor atoms.

Reactions with Thiols. Following the acid−base reactions with organic X−OH compounds, it was also tried to apply X−SH compounds for the same purpose. Various thiols were reacted with $Tp^{Ph,Me}Zn-SH$. Of them *p*-nitrothiophenol (pK_a = 4.6) was found to react like the X−OH acids, reacting in a relatively short time with formation of complex **9a**. Aliphatic thiols did not liberate H_2S under these conditions, in accordance with the fact that their acidity is not higher than that of H_2S. Upon refluxing of the solution for several days, however, they replaced the hydrosulfide ligand by the thiolate ligands. Thus, ethanethiol, 2-propanethiol, and benzyl mercaptan yielded complexes **9b**−**d**.

$Tp^{Ph,Me}Zn\text{-}SR$

9a: R = p-NO_2-C_6H_4
9b: R = C_2H_5
9c: R = i-C_3H_7
9d: R = CH_2-C_6H_5
9e: R = CH_2CH_2-SH
9f: R = $CH_2CH_2CH_2$-SH

The driving force for these reactions must be the gain in entropy resulting from the liberation of H_2S, as the bond energies for Zn−SH and Zn−SR should be very similar. Likewise, entropy arguments can explain why the thioloalkyl complexes **9e,f** do not undergo a second condensation step which would convert them to dinuclear complexes of the type Tp*Zn−S−R′−S−ZnTp*. In this case the entropy gain due to liberation of H_2S would be outweighed by the entropy loss due to the formation of a dinuclear complex. While the reactions leading to **9b**−**f** demonstrate that species other than acids can replace

(27) For structure determinations of compounds containing $(CF_3)_2C(OH)_2$ as a solvate, see: Roesky, H. W.; Lucas, J.; Keller, K.; Dhathathreyan, K. S.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1985**, *118*, 2659. Weber, L.; Buchwald, S.; Ruhlicke, A.; Stammler, H. G.; Neumann, B. *Z. Anorg. Allg. Chem.* **1993**, *619*, 934. Goerlich, J. R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *J. Fluorine Chem.* **1995**, *72*, 69.

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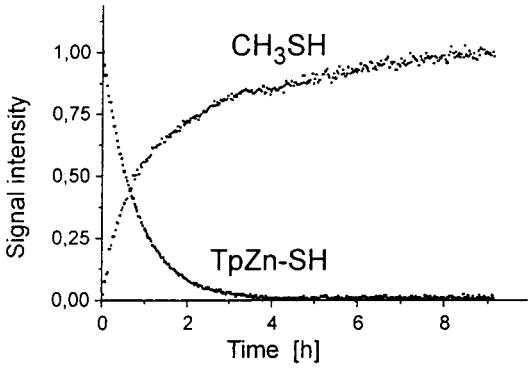

Figure 4. Intensities of the ^{1}H NMR signals for the SH groups of $Tp^{Ph,Me}Zn-SH$ and CH_3SH in $CDCl_3$ at 300 K for starting concentrations of 0.04 M for $Tp^{Ph,Me}Zn-SH$ and 0.40 M for CH_3I.

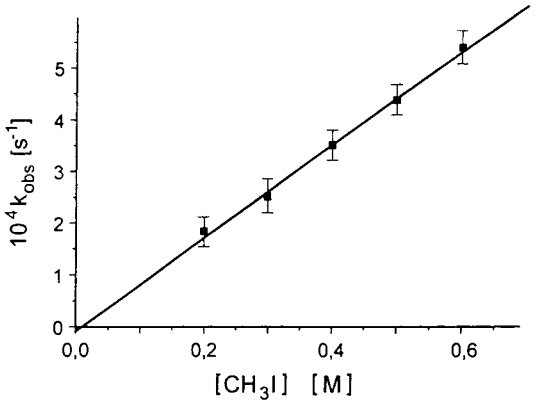

Figure 5. Plot of the k_{obs} values of the $Tp^{Ph,Me}Zn-SH/CH_3I$ reaction versus the CH_3I concentration

the hydrosulfide ligands, they are not the best method to prepare the Tp*Zn−SR complexes, because these are accessible easily from Tp*Zn−OH and the thiols.[20,24,32]

The abundance of reference compounds made the identification of complexes **9** easy. The main spectroscopic feature proving the embedding of the SR ligands between the aromatic groups in 3-position on the pyrazoles is the high-field shift of their NMR signals, as compared to those of the thiols. It amounts to ca. 1 ppm for the SCH_2 protons. This way it was also demonstrated that the free SH units of **9e,f** are not interacting with the zinc centers, in addition to their nature as intact thiols which was confirmed by the observation of their SH NMR signals.

Methylation of $Tp^{Ph,Me}Zn-SH$. The third and most significant way of exploiting the nucleophilicity of the Zn−SH units was found in their alkylation. Alkylating agents convert the zinc-bound hydrosulfide groups to alkanethiols. The unsuitability of the latter as ligands for zinc (no zinc−alkanethiol complex has been described so far) causes their liberation. The anionic constituent of the alkylating agent takes their place as a zinc-bound ligand, and the overall reaction is

$$Tp^*Zn-SH + R-X \rightarrow R-SH + Tp^*Zn-X \qquad (1)$$

We have investigated this reaction type for various Tp*Zn thiolates and varous alkylating agents.[33,34] The accompanying paper[34] describes these reactions and their relevance with respect to biological methylations of thiols by zinc-containing enzymes. In this paper we report the detailed investigation of the reaction between $Tp^{Ph,Me}Zn-SH$ and methyl iodide.

This reaction, cf. eq 1, was found to be clean and quantitative in dichloromethane at room temperature. Removal of all volatiles in vacuo left only $Tp^{Ph,Me}Zn-I$. Thus, the reaction system was suitable for a kinetic study which was performed in $CDCl_3$ at 300 K. Pseudo-first-order conditions were applied by using CH_3I in a 5- to 15-fold excess. The reactions were followed in the NMR by recording the intensities of the SH resonances for $Tp^{Ph,Me}Zn-SH$ and CH_3SH for at least 5 $t_{1/2}$ intervals. Figure 4 shows a representative set of measurement data.

If we take the signal intensities I as a direct measure of the concentration of $Tp^{Ph,Me}Zn-SH$, the pseudo-first-order rate constants k_{obs} were obtained from $\ln(I_t - I_0) = \ln(I_\infty - I_0) - k_{obs}t$. The corresponding log plots (see Supporting Information) for five different excess concentrations of CH_3I are linear to a very good approximation (correlation coefficients > 0.998). From the k_{obs} values the second-order rate constant k'' was obtained according to $k_{obs} = k''[CH_3I]$. Figure 5 shows the corresponding graph which yielded the value of k'' at 300 K as 9.00×10^{-4} M^{-1} s^{-1}, again with a correlation coefficient > 0.998.

The clean second-order reaction, the nonpolar reaction conditions, and the fact that replacement of SH by SR (see above) is at least 2 orders of magnitude slower support the notion that the alkylation occurs at the zinc-bound hydrosulfide. Further measurements will have to verify this by varying the polarity of the medium and the nature of the alkylating reagents as well as of the pyrazolylborate ligands. Using the terminology of nucleophilic substitutions, the reaction is an S_N2 process replacing iodide by hydrosulfide in CH_3I. During this process free iodide may be liberated which then replaces the labile CH_3SH ligand at the zinc ion. However, on the basis of our mechanistic proposals for the nucleophilic reactions of the Tp*Zn−OH complexes,[35] an intramolecular iodide transfer from the methyl group to the Tp*Zn unit may also be envisaged. The S_N2 rate constants for iodide replacement at CH_3I by anionic nucleophiles including thiolates are orders of magnitude larger than the one observed here.[36] This reflects the uncharged nature of the Tp*Zn−SH nucleophile, the lower nucleophilicity of SH^- compared to SR^-, and the steric congestion in the vicinity of the SH ligand. The latter, however, which also implies a hydrophobic, i.e., nonpolar, environment of the SH nucleophile, is yet another reason for an associative, i.e., nonionic, mechanism for the methylation reaction.

Conclusions

It has been shown that Tp*Zn−SH complexes are easy to prepare and easy to handle. Together with Parkin's $Tp^{t-Bu}Zn-SH$[15] and our $Tp^{Cum,Me}Zn-SH$[20] now six such compounds have been described. Other than this class of compounds only two classes of simple metal hydrosulfide complexes have been reported which were accessible in large enough quantities to be subjected to reactivity studies. Angelici worked on the species $[(CO)_5M-SH]^-$ with M = Cr and W,[10] and we investigated the species $(CO)_3(PR_3)_2M-SH$ with M = Mn and Re.[19]

The reactivity studies have shown that the complexes Tp*Zn−SH have little in common with their homologues

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Tp*Zn−OH. The SH ligand is not as good enough a leaving group and not as strong enough a base to allow thiolytic cleavages or nucleophilic additions in analogy to the hydrolytic reactions of Tp*Zn−OH. Neither is the Zn−SH unit a strong enough acid to allow simple deprotonation. The high affinity between zinc and sulfur makes the Zn−SH unit so inert that under certain reaction conditions the detachment of the Tp* ligand from zinc is preferred over interconversions at the Zn−SH function.

The hydrosulfide ligand does undergo substitution reactions when acid−base chemistry is involved. It was shown that X−OH compounds with a pK_a below 7 induce release of H_2S and formation of Tp*Zn−OX. Mechanistically this can be interpreted by an initial protonation, producing the labile H_2S ligand which is then replaced by the OX anion. This holds also when Tp*Zn−SH is reacted with organic thiols. The acid−base situation in this case, however, is such that only very small amounts of $[Tp^*Zn{\cdot}SH_2]^+$ will be produced in the equilibrium mixture. But the release of gaseous H_2S from this mixture is entropically favorable, allowing the SH/SR exchange to go to completion.

Facile electrophilic attack at the sulfur atom is also the initial step of the SH alkylation by methyl iodide. It again produces a labile intermediate $[Tp^*Zn{\cdot}CH_3SH]^+$, which liberates CH_3SH and forms Tp*Zn−I. The mechanistic investigation of this methylation supports the proposal that the alkylation occurs at the zinc-bound and not at the free anionic SH. This is of some relevance for the modeling of zinc enzymes which catalyze alkylation reactions, as discussed in the succeeding paper.[34]

The major difference between the chemistry of Tp*Zn−OH and that of Tp*Zn−SH seems to be the noninvolvement of the zinc ion in reactions of the latter. There are many five coordinate complexes Tp*Zn−(X)(Y) with X and Y being O and N donors, including adducts of Tp*Zn−OH,[35] but there is none for X or Y = S. Likewise the reactions of Tp*Zn−OH with hydrolyzable substrates can be described as involving four-center intermediates containing five-coordinate zinc.[35] This paper has shown that such reactions do not occur with Tp*Zn−SH. Instead, reactions whose primary step involves only electrophilic attack at sulfur take place readily. Thus the general preferences of Zn−S species for lower coordination numbers and of Zn−O species for higher coordination numbers also govern the reactivity of the Zn−OH and Zn−SH complexes discussed here.

Experimental Section

General Data. All experimental techniques and the standard IR and NMR equipment were as described previously.[37] Unless otherwise stated, reactions were carried out in an atmosphere of nitrogen (99.99%) in carefully dried solvents. Starting materials were obtained commercially. The Tp*Zn−OH reagents[20,23,24,38] and $Tp^{Cum,Me}Zn-SH$[20] were prepared as described.

Preparations. $Tp^{Ph,Me}Zn-SH$ (1a). H_2S gas was passed for 15 min through a solution of $Tp^{Ph,Me}Zn-OH$ (1.00 g, 1.76 mmol) in dichloromethane (50 mL). After filtration the solvent was removed in vacuo. Recrystallization from acetonitrile yielded 0.91 g (89%) of **1a** as colorless crystals, mp 198 °C, which lost the cocrystallized acetonitrile in vacuo: ν(BH) 2550 cm^{-1}; ^{1}H NMR ($CDCl_3$) −2.00 [s, 1H, SH], 2.55 [s, 9H, Me(pz)], 6.19 [s, 3H, H(pz)], 7.2−7.7 ppm [m, 15H, Ph].

Anal. Calcd for $C_{30}H_{29}BN_6SZn$ (M_r = 581.9): C, 61.93; H, 5.02; N, 14.44; S, 5.51. Found: C, 62.47; H, 4.92; N, 14.47; S, 5.28.

$Tp^{Py,Me}Zn-SH$ (1b). A procedure was used similar to that for **1a** from $Tp^{Py,Me}Zn-OH$ (1.00 g, 1.76 mmol): yield 0.65 g (63%) of **1b** as colorless crystals, mp 185 °C; ν(BH) 2557 cm^{-1}; ^{1}H NMR ($CDCl_3$) −2.07 [s, 1H, SH], 2.58 [s, 9H, Me(pz)], 6.28 [s, 3H, H(pz)], 7.34 [m, 3H, Py], 7.99 [d, J = 8.0 Hz, 3H, Py], 8.59 [d, J = 4.8 Hz, 3H, Py], 8.76 ppm [s, 3H, Py].

Anal. Calcd for $C_{27}H_{26}BN_9SZn$ (M_r = 584.8): C, 55.45; H, 4.48; N, 21.56; S, 5.48. Found: C, 55.52; H, 4.40; N, 21.60; S, 5.32.

$Tp^{Pic,Me}Zn-SH$ (1c). A procedure was used similar to that for **1a** from $Tp^{Pic,Me}Zn-OH$ (1.00 g, 1.64 mmol). Recrystallization by slow evaporation from acetonitrile/dichloromethane (3:1) yielded 0.76 g (74%) of **1c** as colorless crystals, mp 284 °C (dec): ν(BH) 2552 cm^{-1}; ^{1}H NMR ($CDCl_3$) −2.01 [s, 1H, SH], 2.56 [s, 18H, Me(pz) + Me(py)], 6.23 [s, 3H, H(pz)], 7.18 [d, J = 8.0 Hz, 3 H, Py], 7.87 [dd, J = 8.0 and 2.2 Hz, 3H, Py], 8.63 ppm [d, J = 2.2 Hz, 3H, Py].

Anal. Calcd for $C_{30}H_{32}BN_9SZn$ (M_r = 626.9): C, 57.48; H, 5.14; N, 20.11. Found: C, 57.47; H, 5.20; N, 20.26.

$Tp^{t-Bu,Me}Zn-SH$ (1d). A procedure was used similar to that for **1a** from $Tp^{t-Bu,Me}Zn-OH$ (0.50 g, 0.99 mmol). Recrystallization by slow evaporation from acetonitrile/dichloromethane (3:1) yielded 434 mg (84%) of **1d** as colorless crystals, mp 312 °C (dec): ν(BH) 2574 cm^{-1}; ^{1}H NMR ($CDCl_3$) −0.97 [s, 1H, SH], 1.35 [s, 27H, t-Bu], 2.33 [s, 9H, Me(pz)], 5.77 ppm [s, 3H, H(pz)].

Anal. Calcd for $C_{24}H_{41}BN_6SZn$ (M_r = 521.9): C, 55.23; H, 7.92; N, 16.10. Found: C, 55.25; H, 7.92; N, 16.18.

$Tp^{Pic,Me}Zn-SH{\cdot}2(CF_3)_2C(OH)_2$ (2). Hexafluoroacetone gas was passed for 15 min through a solution of **1c** (200 mg, 0.32 mmol) in dichloromethane/acetonitrile (30 mL) containing about 1% water. The solvents were removed in a stream of nitrogen. Recrystallization from acetonitrile yielded 35 mg (11%) of impure **2** as a partly crystalline colorless material: ν(BH) 2563 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.48 [s, 9H, Me(pz)], 2.59 [s, 9H, Me(py)], 6.15 [s, 3H, H(pz)], 7.25 [m, 3H, Py], 7.90 [m, 3H, Py], 8.70 ppm [m, 3H, Py]; ^{19}F NMR ($CDCl_3$) −85.6 ppm.

Li[$Tp^{Cum,Me}$] (3a). A suspension of $Tp^{Cum,Me}Zn-SH$ (200 mg, 0.28 mmol) and $LiOCH_3$ (15 mg, 0.28 mmol) in diethyl ether (30 mL) was refluxed for 16 h. After evaporation to dryness the residue was extracted with hot acetonitrile (20 mL) and the solution filtered and cooled to −25 °C. A 94 mg (54%) amount of **3a** was precipitated as colorless crystals, mp 199 °C: ν(BH) 2524 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.26 [d, J = 6.9 Hz, 18H, Me(i-Pr)], 2.51 [s, 9H, Me(pz)], 2.91 [sept, J = 6.9 Hz, 3H, CH(i-Pr)], 6.09 [s, 3H, H(pz)], 7.21 [d, J = 8.1 Hz, 6H, Ph], 7.54 ppm [d, J = 8.1 Hz, 6H, Ph].

Anal. Calcd for $C_{39}H_{46}BLiN_6$ (M_r = 616.6): C, 75.97; H, 7.52; N, 13.63. Found: C, 72.94; H, 7.26; N, 13.20.

Na[$Tp^{Cum,Me}$] (3b). A procedure was used similar to that for **3a** from $Tp^{Cum,Me}Zn-SH$ (200 mg, 0.28 mmol) and $NaOCH_3$ (15 mg, 0.28 mmol): yield 127 mg (71%), colorless crystals, mp 195 °C; ν(BH) 2502 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.25 [d, J = 6.9 Hz, 18 H, Me(i-Pr)], 2.47 [s, 9H, Me(pz)], 2.90 [sept, J = 6.9 Hz, 3H, CH(i-Pr)], 6.14 [s, 3H, H(pz)], 7.19 [d, J = 8.2 Hz, 6H, Ph], 7.48 ppm [d, J = 8.2 Hz, 6H, Ph].

Anal. Calcd for $C_{39}H_{46}BN_6Na$ (M_r = 632.6): C, 74.04; H, 7.33; N, 13.28. Found: C, 71.45; H, 7.06; N, 13.50.

DBNH[$Tp^{Ph,Me}$] (3c). A procedure was used similar to that for **3a** from **1a** (200 mg, 0.34 mmol) and DBN (43 mg, 0.34 mmol): yield 98 mg (47%), colorless crystals, mp 161 °C; ν(BH) 2384 cm^{-1}; ^{1}H NMR (CD_3CN) 1.70 [m, 4H, CH_2], 2.09 [s, 9H, Me(pz)], 2.45 [m, 2H, CH_2], 2.96 [m, 2H, NCH_2], 3.07 [m, 2H, NCH_2], 3.16 [m, 2H, NCH_2], 3.58 [s, 1H, NH], 6.31 [s, 3H, H(pz)], 7.2−7.7 ppm [m, 15H, Ph].

Anal. Calcd for $C_{37}H_{41}BN_8$ (M_r = 608.6): C, 73.02, H, 6.79; N, 18.41. Found: C, 72.78; H, 6.88; N, 18.45.

$Tp^{Cum,Me}Zn-C_4H_9$ (4). A procedure was used similar to that for **3a** from $Tp^{Cum,Me}Zn-SH$ (200 mg, 0.28 mmol) and n-BuLi (0.28 mmol = 103 μL of a 2.7 M solution in *n*-heptane): yield 168 mg (81%), colorless powder, mp 141 °C; ν(BH) 2523 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.09 [m, 4H, Zn−CH_2 + Zn−CH_2CH_2], 0.27 [t, J = 7.0 Hz, CH_2CH_3], 0.49 [m, 2H, CH_2CH_3−], 1.25 [d, J = 6.9 Hz, 18H, Me(i-Pr)], 2.51 [s, 9H, Me(pz)], 2.90 [sept, J = 6.9 Hz, 3H, H(i-Pr)], 6.11 [s, 3H, H(pz)], 7.20 [d, J = 8.2 Hz, 6H, Ph], 7.49 ppm [d, J = 8.2 Hz, 6H, Ph].

Anal. Calcd for $C_{43}H_{55}BN_6Zn$ (M_r = 732.2): C, 70.54; H, 7.57; N, 11.48. Found: C, 69.51; H, 7.35; N, 11.37.

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Table 3. Crystallographic Data

	1a	**1b**	**1c**	**2**	**8b**
formula	$C_{30}H_{29}BN_6SZn\cdot CH_3CN$	$C_{27}H_{26}BN_9SZn\cdot 2CH_3CN$	$C_{30}H_{32}BN_9SZn$	$C_{36}H_{36}BF_{12}N_9O_4SZn\cdot CH_3CN$	$C_{35}H_{32}BF_6N_9O_2Zn\cdot CH_3CN$
MW	622.9	666.9	626.9	2031.0	841.9
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4	8	4
a (Å)	12.828(3)	10.902(2)	11.090(2)	19.654(1)	12.135(2)
b (Å)	23.793(5)	15.526(3)	16.370(3)	16.239(1)	20.655(4)
c (Å)	10.912(2)	19.945(4)	16.660(3)	28.215(1)	15.792(3)
α (deg)	90	90	90	90	90
β (deg)	112.22(3)	101.92(3)	91.86(3)	97.788(1)	97.29(3)
γ (deg)	90	90	90	90	90
V (Å^3)	3083.2(1)	3303.2(1)	3022.9(1)	8922.1(6)	3926.1(1)
d(calcd) (g cm^{-3})	1.34	1.34	1.38	1.51	1.42
μ(Mo Kα) (mm^{-1})	0.90	0.85	0.92	0.70	0.70
R1 (obsd reflcns)[a]	0.054	0.068	0.054	0.043	0.051
wR2 (all reflcns)[a]	0.140	0.211	0.223	0.133	0.156

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

Tp^{Ph,Me}Zn−OC$_6$H$_2$(NO$_2$)$_3$ (5). A mixture of **1a** (200 mg, 0.34 mmol) and picric acid hydrate (212 mg, ca. 0.34 mmol) in dichloromethane (20 mL) was stirred for 2 h. Removal of the solvent in vacuo and recrystallization from acetonitrile yielded 192 mg (72%) of **5** as yellow crystals, mp 190 °C: ν(BH) 2545 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.56 [s, 9H, Me(pz)], 6.21 [s, 3H, H(pz)], 7.14 [m, 9H, Ph], 7.46 [m, 6H, Ph], 8.41 ppm [s, 2H, C$_6$H$_2$(NO$_2$)$_3$].

Anal. Calcd for $C_{36}H_{30}BN_9O_7Zn$ (M_r = 776.9): C, 55.66; H, 3.89; N, 16.23. Found: C, 55.52; H, 3.93; N, 16.47.

Tp^{Ph,Me}Zn−OCOPh (6). A procedure was used similar to that for **5** from **1a** (200 mg, 0.34 mmol) and benzoic acid (42 mg, 0.24 mmol) with 48 h of stirring: yield 187 mg (81%) of **6** as colorless crystals, mp 222 °C; ν(BH) 2542 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.55 [s, 9H, Me(pz)], 6.23 [s, 3H, H(pz)], 7.19 [m, 14H, Ph], 7.63 ppm [m, 6H, Ph].

Anal. Calcd for $C_{37}H_{33}BN_6O_2Zn$ (M_r = 669.9): C, 66.34; H, 4.96; N, 12.55. Found: C, 66.09; H, 5.02; N, 12.55.

Tp^{Ph,Me}Zn−OCOCH$_2$Ph (7). A procedure was used similar to that for **5** from **1a** (200 mg, 0.34 mmol) and phenylacetic acid (47 mg, 0.34 mmol) with 48 h of stirring: yield 139 mg (59%) of **7** as colorless crystals, mp 174 °C; ν(BH) 2552 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.52 [s, 9H, Me(pz)], 3.11 [s, 2H, SCH_2], 6.19 [s, 3H, H(pz)], 7.17 [m, 14H, Ph], 7.56 ppm [m, 6H, Ph].

Anal. Calcd for $C_{38}H_{35}BN_6O_2Zn$ (M_r = 683.9) C, 66.73; H, 5.16; N, 12.29. Found: C, 66.65; H, 5.06; N, 12.01.

Tp^{Ph,Me}Zn(hfa) (8a). A mixture of **1a** (200 mg, 0.34 mmol) and hfa (72 mg, 0.34 mmol) in chloroform (50 mL) was refluxed for 72 h. After removal of the solvent in vacuo recrystallization from acetonitrile yielded 221 mg (85%) of **8a** as yellow crystals, mp 234 °C: ν(BH) 2545, ν(CO) 1657 cm^{-1}; ^{1}H NMR($CDCl_3$) 2.48 [s, 9H, Me(pz)], 5.17 [s, 1H, hfa], 6.10 [s, 3H, H(pz)], 7.19 [m, 9H, Ph], 7.35 ppm [m, 6H, Ph]; ^{19}F NMR ($CDCl_3$) −77.3 ppm.

Anal. Calcd for $C_{35}H_{29}BF_6N_6O_2Zn$ (M_r = 755.8): C, 55.62; H, 3.87; N, 11.12. Found: C, 55.39; H, 3.87; N, 11.01.

Tp^{Pic,Me}Zn(hfa) (8b). A procedure was used similar to that for **8a** from **1c** (200 mg, 0.32 mmol) and hfa (66 mg, 0.32 mmol): yield 213 mg of **8b** as yellow crystals, mp 202 °C; ν(BH) 2553, ν(CO) 1657 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.01 [s, 3H, CH_3CN], 2.52 [s, 9H, Me(pz)], 2.56 [s, 9H, Me(py)], 5.39 [s, 1H, hfa], 6.20 [s, 3H, H(pz)], 7.04 [d, J = 8.0 Hz, 3H, Py], 7.53 [m, 3H, Py], 8.51 ppm [d, J = 2.0 Hz, 3H, Py]; ^{19}F NMR ($CDCl_3$) −77.7 ppm.

Anal. Calcd for $C_{35}H_{32}BF_6N_9O_2Zn\cdot CH_3CN$ (M_r = 800.9 + 41.1): C, 52.78; H, 4.19; N, 16.64. Found: C, 52.39; H, 4.11; N, 16.75.

Tp^{Ph,Me}Zn−SC$_6$H$_4$-*p*-NO$_2$ (9a). A mixture of **1a** (200 mg, 0.34 mmol) and *p*-nitrothiophenol (53 mg, 0.34 mmol) in dichloromethane (30 mL) was refluxed for 16 h. After removal of the solvent in vacuo, recrystallization from acetonitrile yielded 134 mg (55%) of **9a** as yellow crystals, mp 214 °C: ν(BH) 2553 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.58 [s, 9H, Me(pz)], 6.20 [s, 3H, H(pz)], 6.37 [d, J = 9.0 Hz, 2H, C$_6$H$_4$], 7.12 [m, 11H, Ph + C$_6$H$_4$], 7.53 ppm [m, 6H, Ph].

Anal. Calcd for $C_{36}H_{32}BN_7O_2SZn$ (M_r = 703.0): C, 61.51; H, 4, 59; N, 13.95; S, 4.56. Found: C, 61.52; H, 4.64; N, 14.00; S 4.37.

Tp^{Ph,Me}Zn−SC$_2$H$_5$ (9b). A mixture of **1a** (200 mg, 0.34 mmol) and C_2H_5SH (1.19 g, 19.2 mmol) in chloroform (30 mL) was refluxed for 72 h. After removal of the solvent in vacuo, recrystallization from acetonitrile yielded 127 mg (61%) of **9b** as colorless crystals, mp 269 °C: ν(BH) 2551 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.24 [t, J = 7.0 Hz, 3H, CH_3(Et)], 1.00 [q, J = 7.0 Hz, 2H, CH_2(Et)], 2.47 [s, 9H, Me(pz)], 6.11 [s, 3H, H(pz)], 7.25 [m, 9H, Ph], 7.67 ppm [m, 6H, Ph].

Anal. Calcd for $C_{32}H_{33}BN_6SZn$ (M_r = 609.9): C, 63.02; H, 5.45; N, 13.78. Found: C, 62.92; H, 5.49; N, 13.87.

Tp^{Ph,Me}Zn−SCH(CH$_3$)$_2$ (9c). A procedure was used similar to that for **9b** from **1a** (200 mg, 0.34 mmol) and $(CH_3)_2CHSH$ (1.22 g, 16.0 mmol): yield 122 mg (57%), colorless crystals, mp 250 °C; ν(BH) 2549 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.28 [d, J = 6.6 Hz, 6H, CH_3(i-Pr)], 1.46 [sept, J = 6.6 Hz, 1H, CH(i-Pr)], 2.55 [s, 9H, Me(pz)], 6.17 [s, 3H, H(pz)], 7.37 [m, 9H, Ph], 7.69 ppm [m, 6H, Ph].

Anal. Calcd for $C_{33}H_{35}BN_6SZn$ (M_r = 624.0): C, 63.53; H, 5.65; N, 13.47; S, 5.14. Found: C, 63.27; H, 5.83; N, 13.53; S, 5.08.

Tp^{Ph,Me}Zn−SCH$_2$C$_6$H$_5$ (9d). A procedure was used similar to that for **9b** from **1a** (200 mg, 0.34 mmol) and $C_6H_5CH_2SH$ (945 mg, 7.6 mmol): yield 126 mg (53%), colorless crystals, mp 189 °C; ν(BH) 2536 cm^{-1}; ^{1}H NMR($CDCl_3$) 1.52 [s, 2H, H_2O], 2.20 [s, 2H, CH_2], 2.56 [s, 9H, Me(pz)], 6.20 [s, 3H, H(pz)], 6.35 [m, 2H, benzyl], 6.96 [m, 3H, benzyl], 7.38 [m, 9H, Ph], 7.77 ppm [m, 6H, Ph].

Anal. Calcd for $C_{37}H_{35}BN_6SZn\cdot H_2O$ (M_r = 672.0 + 18.0): C, 64.41; H, 5.40; N, 12.18. Found: C, 64.56; H, 5.17; N, 12.40.

Tp^{Ph,Me}Zn−SCH$_2$CH$_2$SH (9e). A procedure was used similar to that for **9a** from **1a** (250 mg, 0.43 mmol) and $HSCH_2CH_2SH$ (891 mg, 9.5 mmol): yield 119 mg (43%), colorless crystals, mp 118 °C; ν(BH) 2551 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.59 [t, J = 8.2 Hz, 1H, SH], 1.08 [m, 2H, CH_2], 1.43 [m, 2H, CH_2], 2.48 [s, 9H, Me(pz)], 6.11 [s, 3H, H(pz)], 7.32 [m, 9H, Ph], 7.60 ppm [m, 6H, Ph].

Anal. Calcd for $C_{32}H_{33}BN_6S_2Zn$ (M_r = 642.0): C, 59.87; H, 5.18; N, 13.09. Found: C, 59.73; H, 5.09; N, 13.05.

Tp^{Ph,Me}Zn−SCH$_2$CH$_2$CH$_2$SH (9f). A procedure was used similar to that for **9a** from **1a** (250 mg, 0.43 mmol) and $HSCH_2CH_2CH_2SH$ (928 mg, 8.6 mmol): yield 217 mg (77%), colorless crystals, mp 252 °C; ν(BH) 2559 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.85 [m, 5H, SH, CH_2, CH_2], 1.73 [m, 2H, CH_2], 2.47 [s, 9H, Me(pz)], 6.10 [s, 3H, H(pz)], 7.31 [m, 9H, Ph], 7.63 ppm [m, 6H, Ph].

Anal. Calcd for $C_{33}H_{35}BN_6S_2Zn$ (M_r = 656.0): C, 60.42; H, 5.38; N, 12.81. Found: C, 60.16; H, 5.13; N, 13.04.

Methylation of Tp^{Ph,Me}Zn−SH. A solution of **1a** (100 mg, 0.17 mmol) in dichloromethane (20 mL) was treated with 0.4 mL (900 mg, 6.0 mmol) of methyl iodide. After the solution was stirring for 14 h, the volatile materials were removed in vacuo. The remaining, partly crystalline residue consisted of 115 mg (99%) of Tp^{Ph,Me}Zn−I,[39] which was spectroscopically pure.

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Kinetic Measurements. The standard solutions of complex **1a** and methyl iodide in $CDCl_3$ (99.99%) were kept in the dark. All reagents and the cavity of the NMR spectrometer were thermostated to 300.0 K before the measurements. The reagents were combined immediately prior to the measurements. The concentrations of the reagents were adjusted to 0.04 M for **1a** for all five measurements and to 0.20, 0.30, 0.40, 0.50, and 0.60 M for CH_3I, respectively. The intensities of the ^1H NMR resonances of the SH protons of **1a** and of CH_3SH were recorded automatically every 60 s and stored for digital data processing. Each kinetic run was repeated two times, and the data were reproducible within 5%. The averaged data were used for the calculations. The resulting K_{obs} values for 0.20, 0.30, 0.40, 0.50, and 0.60 M CH_3I were 1.82×10^{-4}, 2.50×10^{-4}, 3.49×10^{-4}, 4.37×10^{-4}, and 5.38×10^{-4} s^{-1}, respectively.

Structure Determinations. The crystals were taken as obtained from the reactions. The data sets were obtained at 200 K with a Bruker AXS Smart CCD diffractometer and treated without an absorption correction. The structures were solved with direct methods and refined anisotropically using the SHELX program suite.[40] 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.[41] Table 3 lists the crystallographic data.

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

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