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Tris(thioimidazolyl)borate-Zinc-Thiolate Complexes for the Modeling of Biological Thiolate Alkylations

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The S_3Zn–SR coordination of thiolate-alkylating enzymes such as the Ada DNA repair protein was reproduced in tris(thioimidazolyl)borate-zinc-thiolate complexes $Tti^RZn–SR'$. Four different Tti^R ligands and nine different thiolates were employed, yielding a total of 12 new complexes. In addition, one $Tti^RZn–SH$ complex and two thiolate-bridged $[Tti^R\text{-}SEt\text{-}Tti^R]^+$ complexes were obtained. A selection of six thiolate complexes was converted with methyl iodide to the corresponding methyl thioethers and $Tti^RZn–I$. According to a kinetic analysis these reactions are second-order processes, which implies that the alkylations are likely to occur at the zinc-bound thiolates. They are much faster than the alkylations of zinc thiolates with N_3 or N_2S tripod ligands. The most reactive thiolate, $Tti^{Xyl}Zn–SEt$, reacts slowly with trimethyl phosphate in a nonpolar medium at room temperature, yielding methyl-ethyl-thioether and $Tti^{Xyl}Zn–OPO(OMe)_2$ which can be converted back to the thiolate complex with NaSEt. This is the closest reproduction of the Ada repair process so far.

Introduction

This is the fourth paper in our series on alkylations of zinc-bound thiolates in (tripod)Zn−SR complexes. In the previous papers the tripods used were offering N_3,[1] N_2S,[2] and NS_2 donor sets.[3] Here the tripods are tris(thioimidazolyl)-borates, abbreviated Tti^R, which offer a S_3 donor set.

The motivation for this work comes from the fact that Nature uses quite a number of zinc enzymes to perform thiolate alkylations for various purposes,[4] the most prominent of which are cobalamin-independent methionine synthase[5] and the Ada DNA repair protein.[6] In these enzymes zinc is attached to the protein via histidine and cysteine in N_2S, NS_2, or S_3 donor environments, and it is generally believed that the reacting thiolate is bound to zinc in order to facilitate its alkylation.

The purpose of our work is to gather some mechanistic information on the alkylation of zinc-bound thiolates and to find out why Nature uses the unusual sulfur-rich donor environment for the zinc ion in the enzymes. For this purpose we have varied the "protein substitute" in the form of tripodal pyrazolylborate-derived N_3, N_2S, NS_2, and S_3 ligands, the zinc-bound thiolates from SH via S-alkyl, S-benzyl, S-aryl, S-nitroaryl, and S-pentafluoroaryl to S-cysteinyl and S-homocysteinyl, and we have varied the alkylating agents from alkyl halides via dialkyl sulfates and trialkyl phosphates to quarternary ammonium salts.

In the three previous papers[1−3] we have listed the relevant literature on the biochemical background and completely cited all the work of our competitors, the leading ones among which are G. Parkin, C. Carrano, and C. Riordan. The subject of this paper, the alkylation of (S_3)Zn-thiolates, has been touched upon by Lippard[7,8] (in a detailed study modeling the Ada repair protein using $Zn(SPh)_4^{2-}$), by Parkin[4,9,10] (alkylation of $Tti^{Ph}Zn−SPh$ and $Tti^RZn−SCH_2CONHPh$), and by Riordan[11] (preparation of $TtZn−SPh$). In almost all previous studies the methyl iodide reactions of tripod-zinc-

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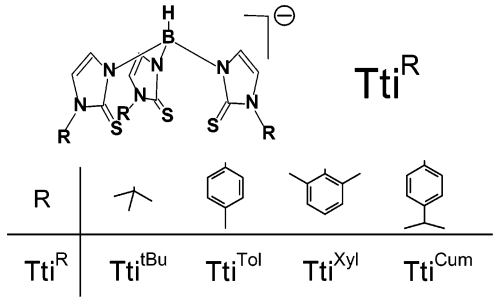
thiolates were found to be second-order processes, in accordance with the assumption that the thiolate is alkylated in the zinc-bound state. Only for the reaction of $Zn(SPh)_4^{2-}$ with trimethyl phosphate in the very polar solvent DMSO was it found that thiophenolate dissociates from zinc prior to alkylation.

Based on the previous knowledge, our alkylation studies of the Tti^RZn-SR complexes therefore could be expected to yield two new pieces of information, first whether the ZnS_4 coordination in these compounds facilitates dissociation, leading to the alkylation of the free thiolates, and second whether the observed increase of the rate of alkylation with increasing sulfur content in the ligand sphere[1−3] is maintained here, which would make the Tti^RZn-thiolates the most reactive substrates of alkylation. We tested these hypotheses using a complete range of different thiolates which were attached to zinc bearing the four different Tti^R ligands shown below.



Results and Discussion

Preparations. The standard procedure for making the thiolate complexes **1a**−**1l** was to combine the potassium salt of Tti^R first with zinc nitrate or zinc perchlorate, generating in situ $Tti^RZn-ONO_2$ or $Tti^RZn-OClO_3$,[12,13] and then adding a solution of the sodium thiolate. Alternatively, the zinc thiolate could be generated first and then treated with $KTti^R$. The latter procedure worked only with the electron-poor thiolates. The ethyl and isopropyl thiolate complexes **1a** and **1b** turned out to be the most difficult to prepare, as already observed for the NS_2 tripod ligands.[3] The key to success here was using a considerable excess of the thiolate and applying dilution techniques, i.e., dropping the thiolate solution very slowly into the $Tti^RZn-OClO_3$ solution. To avoid the common dismutation reaction forming $Zn(Tti^R)_2$ and $Zn(SR)_2$,[3,14] all reactions had to be performed at or below room temperature.

Tti^RZn-SR′	R	R′
1a	Xyl	C_2H_5
1b	Xyl	*i*-C_3H_7
1c	Xyl	$CH_2C_6H_5$
1d	Xyl	$CH_2CH_2C(COOEt)(NHAc)$
1e	Xyl	$CH_2CH_2NH(tBoc)$
1f	Xyl	C_6H_5
1g	Xyl	$C_6H_3(o\text{-}CH_3)_2$
1h	Xyl	$C_6H_4(p\text{-}NO_2)$
1i	tBu	$C_6H_4(p\text{-}NO_2)$
1j	Tol	$C_6H_4(p\text{-}NO_2)$
1k	Cum	$C_6H_4(p\text{-}NO_2)$
1l	Xyl	C_6F_5

Initial attempts to obtain a $Tti^RZn-SEt$ complex unexpectedly produced the two singly thiolate-bridged complexes **2a** and **2b**. They represent a hitherto unknown structural type in this field of pyrazolylborate-derived tripod-Zn-X complexes, with X being OH, OR, SH, or SR, and tripods with N_3, N_2S, NS_2, or S_3 donor sets. Their formation seems to be an expression of the high electron density at the ethanethiolate sulfur in **1a** and the like, making complex **2a** an adduct of **1a** to the $[Tti^{Xyl}Zn]^+$ fragment. Actually, the ability of the latter to accept neutral sulfur donors was already observed by us[14] and Parkin[4] using thioimidazolines.

$$[Tti^RZn-SEt-ZnTti^R]ClO_4$$
2a: R = Xyl, **2b**: R = t-Bu

Finally the basic complex of the series, the hydrosulfide **3a**, could be obtained by treating the in situ generated hydroxide $Tti^{Xyl}Zn-OH$ with hydrogen sulfide. **3a**, which is stable at room temperature, complements our $Tp^{Ph,Me}Zn-SH$[15] and Parkin's $Tti^{t-Bu}Zn-SH$[10] complexes. Like all other related L·Zn−SH complexes[10,15−17] it does not show a typical SH band in its IR spectrum but the characteristic ^1H NMR resonance at −1.69 ppm.

$$Tti^{Xyl}Zn-SH$$
3a

Structures. Previously the structures of $Tti^{t-Bu}Zn-SH$ (Zn−S = 2.27 Å)[10] and of two $Tti^RZn-SPh$ complexes (Zn−S = 2.26[9] and 2.27 Å[10]) had been reported. We determined the structures of **1a**, **1c**, **1e**, **1f**, **1h**, **1k**, **1l**, **2a**, **2b**, and **3a**. Of the terminal thiolate complexes **1**, those of **1a** and **1e** are shown in Figures 1 and 2. Details of the others are given in the Supporting Information.

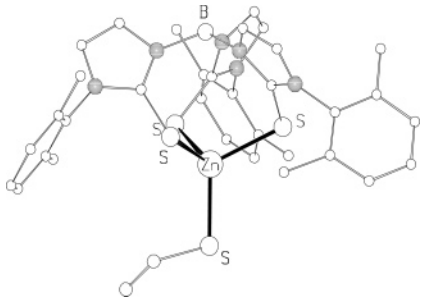


Figure 1. Molecular structure of $Tti^{Xyl}Zn-SEt$ (**1a**).

The geometrical details of the Tti^R ligands in these complexes vary little, e.g. the Zn−S distances all range within 2.36 ± 0.03 Å; hence, only the features of the thiolate ligands are worth discussing. Of these the Zn−S bond lengths also show a rather small spread. As Table 1 shows, they range from 2.25 to 2.30 Å in the terminal thiolate complexes.

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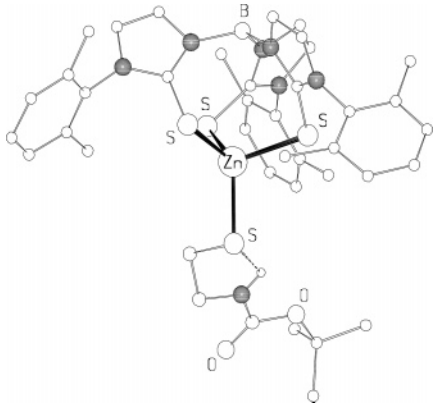

Figure 2. Molecular structure of Tti^{Xyl}Zn−SCH$_2$CH$_2$NH(tBoc) (**1e**).

Table 1. Zn−S Bond Lengths (Å) for the Thiolate Ligands in Complexes **1**, **2,** and **3**

1a	2.268(1)	**1k**	2.279(2)
1c	2.253(3)	**1l**	2.301(1)
1e	2.266(2)	**2a**	2.311(3)/2.326(3)
1f	2.248(2)	**2b**	2.332(3)/2.318(3)
1h	2.301(1)	**3a**	2.258(1)

There is just a slight tendency for the aliphatic thiolates to make shorter Zn−S bonds than the aromatic ones. Altogether, however, there is a dependency of the Zn−S(thiolate) distances on the nature of the tripod ligands. For the tris(pyrazolyl)borate complexes this distance averages near 2.20 Å,[18] for the bis(pyrazolyl)thioimidazolyl borate complexes it is near 2.23 Å,[2] and the two reported (pyrazolyl)bis(thioimidazolyl)borate-zinc-*p*-nitrothiophenolates have Zn−S bond lengths (2.28 Å) which are about 0.01−0.02 Å shorter than the bonds in **1h** and **1k**. The average of all Zn−S(thiolate)bond lengths for complexes **1** (2.27 Å) is clearly the largest among the four groups of compounds.

The structure of **1e** is shown here because it displays a feature that may be of some relevance in biological thiolate alkylations.[4] Its aminoethanethiolate ligand can (and does) fold back in a favorable way to make a N−H···S hydrogen bond. This is evident in **1e** by a N···S distance of 3.11 Å, despite the fact that the NH hydrogen atom was not located crystallographically. Similar S−C−C−NH arrangements have been observed by Riordan,[19] Carrano,[20] and Parkin[4] in (tripod)Zn−SR complexes and found to affect the rate of thiolate alkylation (see discussion below).

The unexpected isolation of the Zn−SR−Zn complexes **2a** and **2b** was a first indication of the very high electron density (viz. nucleophilicity) at the ethanethiolate sulfur in **1a**. The identity of **2a** and **2b**, which represent a new structural type in the (tripod)Zn-X field, was resolved by their structure determinations, of which the one of **2b** was of rather low quality and will not be discussed here. Figure 3 shows the structure of **2a**. While there are, again, no unusual features in the Tti^R ligands (average Zn−S distance

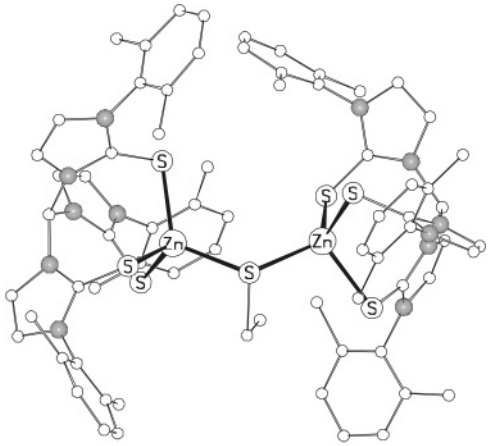

Figure 3. Molecular structure of the dinuclear cation of [Tti^{Xyl}Zn−SEt-ZnTti^{Xyl}]ClO$_4$ (**2a**).

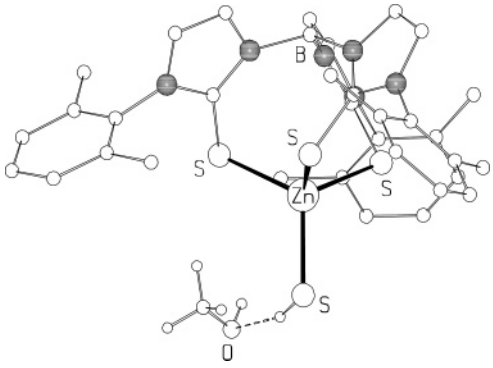

Figure 4. Molecular structure of Tti^{Xyl}Zn−SH·CH$_3$OH (**3a**).

2.34 Å in **2a**), the Zn−S(thiolate) distances (2.311(3) and 2.326(3) Å in **2a**) are characteristically longer than the distances in **1a** with terminal ethanethiolate. The Zn−S−Zn angle of 130.0(2) Å in **2a** is rather large, most likely representing intramolecular repulsions between the two Tti ligands. We are not aware of any other zinc complex with a singly bridged Zn_2S_7 arrangement, but the related Zn_2Cl_7 arrangement has been observed in a ring-shaped $Zn_{10}Cl_{20}$ oligomer with bridging polydentate nitrogen ligands.[21]

The structure of the hydrosulfide complex **3a** (see Figure 4) fits in very well with those of the other mononuclear complexes. The Zn−S bond length of 2.26 Å, which is among the shortest of the Zn−S bond lengths reported here corresponds with that reported by Parkin for Tti^{tBu}Zn−SH (2.27 Å).[10] Crystalline **3a** retains one molecule of the crystallization solvent methanol. It is attached by a S−H···O hydrogen bond to the hydrosulfide ligand, resulting in a S···O distance of 3.34 Å. In this respect complex **3a** closely resembles the methanol adduct of Tp^{Cum,Me}Zn−OH.[17] Its pyrazolylborate analogue Tp^{Ph,Me}Zn−SH, however, does not retain methanol upon crystallization.[15]

Methyl Iodide Reactions. Like in the previous parts of this investigation[1−3] a selected set of the thiolate complexes was chosen for alkylation reactions, ranging from the most electron-rich alkanethiolate to the most electron-poor *p*-nitrothiophenolate and including the biologically relevant

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homocysteinate **1d** as well as the internally hydrogen-bonded **1e**. All reactions proceeded smoothly in chloroform at room temperature according to eqs 1 and 2. The resulting $Tti^{R}Zn$-iodide complexes **4a** and **4b** were isolated as well as the methyl thioethers (except for $CH_3SC_2H_5$) which were identified by ^1H NMR as being the only reaction products in solution.

$$\underset{\textbf{1a, c, d, e, f, h}}{Tti^{Xyl}Zn-SR} + CH_3I \rightarrow \underset{\textbf{4a}}{Tti^{Xyl}ZnI} + CH_3SR \qquad (1)$$

$R = C_2H_5$, $CH_2C_6H_5$, $CH_2CH_2CH(NHAc)(COOEt)$, $CH_2CH_2NH(t\text{-}Boc)$, C_6H_5, $p\text{-}NO_2C_6H_4$

$$\underset{\textbf{1j}}{Tti^{Tol}Zn-SC_6H_4NO_2} + CH_3I \rightarrow \underset{\textbf{4b}}{Tti^{Tol}ZnI} + CH_3SC_6H_4NO_2 \qquad (2)$$

The alkylations were found to be the fastest in the (tripod)-Zn−SR series,[1−3] several orders of magnitude faster than those of Tp*Zn−SR[1] and still significantly faster than those of the (NS_2 tripod)Zn thiolates.[3] The ethanethiolate **1a** was consumed in less than a minute at room temperature, the thiophenolate **1f** within 10 minutes, and the methylation of the *p*-nitrothiophenolates **1h** and **1j** took only hours to come to completion. As observed before for related systems,[4,19] intramolecular hydrogen bonding slows down the alkylation process: the aminoethanethiolate **1e** was found to react about one third as fast as the ethanethiolate **1a**. The biological relevance of this observation may lie in the selectivity of enzymatic thiolate alkylations: in the enzymes the catalytic zinc is attached to the protein by at least one cysteinate sulfur, but Nature has ensured that during thiolate alkylation this cysteinate is not attacked.

The smoothness of the alkylation reactions and the nonpolar reaction conditions provide circumstantial evidence that the reactions are nonionic, i.e., the thiolates are alkylated in the zinc-bound state. We are in the midst of a comprehensive kinetic study aimed at providing proof of this for all alkylations in Zn−SR complexes with N_3, N_2S, NS_2, and S_3 tripod ligands, the results of which are to be published in a separate paper. Of the thiolate complexes dealt with here, the *p*-nitrothiophenolates **1h** and **1j** allowed a kinetic study by ^1H NMR on a convenient time scale. As usual[2,3] treating them with large excesses of CH_3I in $CDCl_3$ at 300 K and recording suitable ^1H NMR signal intensities of both the starting complex and the thioether during the reaction allowed us to obtain the pseudo-first-order rate constants k_{obs}. Recording the data sets several times produced good fits, as evidenced for the methylation of **1h** by Figure 5.

From the plots of the resulting k_{obs} values against the corresponding CH_3I concentrations the regression lines were obtained whose slope defines the second-order rate constants k''. The k'' values, thus extracted, are $2.2(3) \times 10^{-3}$ M^{-1} s^{-1} for **1h** and $8.6(5) \times 10^{-3}$ M^{-1} s^{-1} for **1j**. These rate constants are of the same size as that for the methylation of the benzylthiolate-zinc complex of the N_2S tripod.[2] Considering the qualitative observation made here that the benzylthiolate **1c** reacts around 300 times faster than the *p*-nitrothiophenolate **1h**, one can state that the rate increase from the $(N_2S)Zn-SR$ units to the $(S_3)Zn-SR$ units is about 2 orders of magnitude. Yet both the observations that the $(N_2S)Zn$-thiolates do not react faster than the $(N_3)Zn$-thiolates[1,2] and that **1h** and **1j** do not react much faster than the *p*-nitrothiophenolates of the $(NS_2)Zn$ unit[3] call for a more thorough and comprehensive kinetic investigation. We hope to complete this investigation soon.

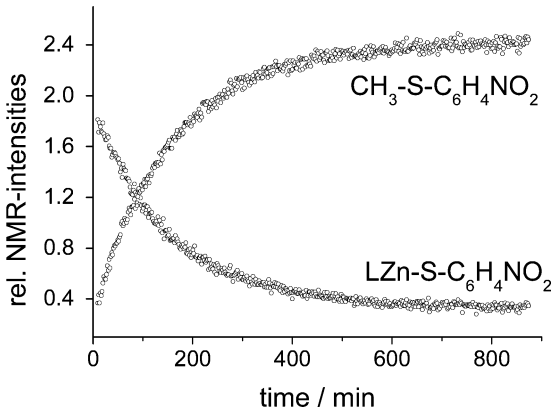

Figure 5. Intensities of one of the two $C_6H_4NO_2$ ^1H NMR signals of **1h** and of $CH_3SC_6H_4NO_2$ in $CDCl_3$ at 300 K for starting concentrations of 0.010 M for **1h** and 0.10 M for CH_3I.

Trimethyl Phosphate Reactions. Until now the use of trimethyl phosphate as an alkylating agent for zinc thiolates had required very polar solvents (typically DMSO) and normally prolonged heating.[2,3,8,22] As a consequence the alkylation mechanism changed to the reaction of ionic thiolate, as revealed for the treatment of $Zn(SPh)_4^{2-}$ with $PO(OMe)_3$.[8] The high nucleophilic strength of the ethanethiolate complex **1a** now allowed us to carry out the trimethyl phosphate reaction at room temperature in chloroform. It proceeded very slowly, taking several weeks to come to completion. Yet the nonpolar conditions as well as the clean and quantitative reaction forming methyl ethyl thioether and the phosphate complex **5** correspond strictly to the observations for the methyl iodide reactions, thereby indicating that the methylation by trimethyl phosphate occurs in the same way. This may mean that the thiolate is again alkylated in the zinc-bound state. Yet again a thorough kinetic investigation is called for to verify this.

$$\underset{\textbf{5}}{Tti^{Xyl}Zn-OPO(OCH_3)_2}$$

Complex **5** was identified by a structure determination (see Figure 6). It is the first methyl phosphate complex of a tripod zinc unit that we have determined. But its structural features compare favorably with those of the many Tp*Zn-organophosphate complexes investigated by us.[23] Characteristically the two "nonorganic" P−O bonds are of equal length, prohibiting the distinction between P═O and P−O−Zn, and the Zn−O−P angle is rather large.

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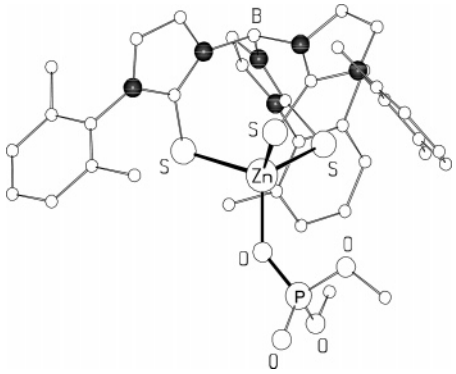

Figure 6. Molecular structure of Tti^{Xyl}Zn−OPO(OMe)$_2$ (**5**). Relevant bond lengths (Å) and angles (°): Zn−O 1.925(4), P−O(Zn) 1.496(4), P−O 1.472(5), P−OMe 1.567(5) and 1.583(5), Zn−O−P 138.8(3).

To reproduce the catalytic cycle of the Ada DNA repair protein in a stoichiometric fashion, we tried to revert the phosphate complex **5** to the thiolate complex **1a**. This proved to be possible using a 50% excess of $NaSC_2H_5$, while with an equimolar amount of thiolate again the dinuclear complex **2a** was formed. Considering that a buffered aqueous solution of ethanethiol contains equilibrium concentrations of the thiolate, one can propose that in an appropriate mixture complex **1a** (or a predecessor thereof in the form of a OH or OH_2 complex) might act as a catalyst for thiolate alkylation by organophosphates. This, even in the stoichiometric reactions observed here, represents the closest modeling of the Ada repair process so far.

Conclusions

This paper completes our series of investigations on the alkylation of zinc thiolates with scorpionate ligands. In all four donor environments (N_3, N_2S, NS_2, S_3) the uncharged molecular L·Zn−SR species were found to be of sufficient nucleophilicity to undergo facile reactions with methyl iodide in nonpolar media. In all cases these reactions were of the S_N2 type, which supports the assumption that the thiolates are alkylated in the zinc-bound state.

The TtiZn−SR complexes examined in the present work are the most reactive ones in the series. They confirm the observation that the Zn−SR nucleophilicity is proportional to the number of sulfur donors on the scorpionate ligands. However, the available kinetic data do not show a steady progression of reactivities along the $N_3\cdots S_3$ series. The reason for this is probably an irregular variation of the steric situation around the Zn−SR centers in the available complexes.

The trends in reactivity of our Zn−SR complexes are in line with the coordination environment of the zinc ions in the thiolate-alkylating enzymes. Most of these enzymes have a sulfur-rich coordination of zinc, most commonly (NS_2)Zn-X, and the catalytic center of the Ada DNA repair protein is a $Zn(SR)_4^{2-}$ unit. It suggests itself that coordination of zinc by sulfur donors (cysteinate in the enzymes, thioimidazolate in the model complexes) is the most efficient way to increase its electron density and hence the nucleophilicity of the zinc-bound thiolate substrates.

It was gratifying to find not only that complexes **1** reproduce the ZnS_4 coordination pattern of the Ada DNA repair protein, but that their most reactive representative **1a** is also the first model complex that can dealkylate an alkyl phosphate at room temperature in nonpolar media. The facile reconversion of the resulting (S_3)Zn-phosphate complex **5** to the (S_3)Zn-thiolate complex **1a** has enabled us to present the first stoichiometric equivalent of the complete catalytic cycle of the Ada DNA repair process.

Experimental Section

General Data. All experimental techniques and the standard IR and NMR equipment were as described previously.[24] The Tti^R ligands[12,13] and the NAc and OEt protected homocysteine[25] were prepared according to the published procedures. All other organic reagents were bought from Merck. The sodium thiolates were prepared in situ from the thiols and a 0.25 M stock solution of $NaOCH_3$.

The ^{1}H NMR spectral data for the Tti^R ligands in the new complexes vary only negligibly between themselves and the reference compounds.[12,13] Therefore, only the data for the coligands X in the Tti^{R}Zn−X complexes are reported here. A frequent problem with the elemental analyses of this kind of complexes is that the carbon values are outside the accepted range. When this was the case here, at least one additional analysis value (S, Zn) was determined.

1a. A solution of $NaSC_2H_5$, made up from 32 mg (37.7 μL, 0.51 mmol) of C_2H_5SH and 2 mL (0.5 mmol) of the $NaOCH_3$ stock solution, in 20 mL of methanol was added dropwise and very slowly to a solution of 0.11 g (0.30 mmol) of $Zn(ClO_4)_2\cdot 6H_2O$ and 0.20 g (0.30 mmol) of KTti^{Xyl} in 50 mL of methanol. After 24 h of stirring the volume of the solution was reduced to 10 mL in vacuo, filtered, and evaporated to dryness. The residue was dissolved in 10 mL of dichloromethane, filtered, and evaporated to dryness again. Crystallization from methanol/dichloromethane (3:1) yielded 112 mg (49%) of **1a** as colorless crystals, mp 270 °C (dec), ν(BH) 2458 cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.04 [t, J = 7.2 Hz, 3H, CH_3(SEt)], 2.31 [q, J = 7.2 Hz, 2H, CH_2(SEt)]. Anal. Calcd for $C_{35}H_{39}BN_6S_4Zn$ (M_r = 748.20): C, 56.19; H, 5.25; N, 11.23; S, 17.14; Zn, 8.74. Found: C, 54.88; H, 5.17; N, 11.66; S, 16.51; Zn, 8.42.

1b. Like **1a** from 39 mg (47.6 μL, 0.30 mmol) of *i*-C_3H_7SH, 0.11 g (0.30 mmol) of $Zn(ClO_4)_2\cdot 6H_2O$ and 0.20 g (0.30 mmol) of KTti^{Xyl}. Yield 154 mg (65%) of **1b** as colorless crystals, mp 210 °C (dec). ν(BH) 2413 cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.08 [d, J = 6.6 Hz, 6H, CH_3(i-Pr)], 2.82 [sept, J = 6.6 Hz, 1H, CH(i-Pr)]. Anal. Calcd for $C_{36}H_{41}BN_6S_4Zn$ (M_r = 762.23): C, 56.73; H, 5.42; N, 11.03; S, 16.83; Zn, 8.58. Found: C, 55.79; H, 5.32; N, 11.05; S, 16.02; Zn, 8.17.

1c. Like **1a** from 37 mg (36 μL, 0.30 mmol) of $C_6H_5CH_2SH$, 0.11 g (0.30 mmol) of $Zn(ClO_4)_2\cdot 6H_2O$, and 0.20 g (0.30 mmol) of KTti^{Xyl}. Yield 168 mg (69%) of **1c** as colorless crystals, mp 195 °C (dec). ν(BH) 2438 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.51 [s, 2H, CH_2(benzyl)]. Anal. Calcd for $C_{40}H_{41}BN_6S_4Zn\cdot CH_2Cl_2$ (M_r = 810.27 + 84.93): C, 55.01; H, 4.84; N, 9.39; S, 14.33; Zn, 7.30. Found: C, 54.89; H, 4.94; N, 9.77; S, 14.33; Zn, 7.31.

1d. The sodium salt of $HSCH_2CH_2C(COOEt)(NHAc)$ was prepared by combining 0.12 g (0.60 mmol) of *N*-acetyl homocysteine ethyl ester and 2.4 mL (0.6 mmol) of the NaOMe stock

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solution in 15 mL of methanol. This solution was added dropwise to a solution of 0.11 g (0.30 mmol) of $Zn(ClO_4)\cdot 6H_2O$ and 0.20 g (0.30 mmol) of $KTti^{Xyl}$ in 35 mL of methanol. After 3 d of stirring the solution was evaporated to dryness at 40 °C. The residue was extracted with 20 mL of dichloromethane, filtered, and evaporated to dryness again. Crystallization from methanol/dichloromethane (3:1) yielded 134 mg (50%) of **1d** as colorless crystals, mp 205 °C (dec). ν(BH) 2437 cm^{-1}. ^1H NMR ($CDCl_3$): 1.05 [m, 4H, CH_2], 1.23 [t, $J = 7.2$ Hz, 3H, CH_3(Et)], 1.85 [s, 3H, CH_3(Ac)], 2.69 [m, 1H, CH], 4.14 [q, $J = 7.2$ Hz, 2H, CH_2(Et)], 4.78 [m, 1H, NH]. Anal. Calcd for $C_{41}H_{49}BN_7O_3S_4Zn$ ($M_r = 892.35$): C, 55.19; H, 5.53; N, 10.99; S, 14.37; Zn, 7.33. Found: C, 53.37; H, 5.48; N, 10.75; S, 14.10; Zn, 7.19.

1e. Like **1d** from 76 mg (0.45 mmol) of *tert*-butyl-N(2-mercaptoethyl) carbamate, 0.11 g (0.30 mmol) of $Zn(ClO_4)\cdot 6H_2O$, and 0.20 g (0.30 mmol) of $KTti^{Xyl}$. Yield 115 mg (44%) of **1e** as colorless crystals, mp 210 °C (dec). ν(BH) 2439 cm^{-1}. ^1H NMR ($CDCl_3$): 1.39 [s, 9H, t-Bu], 2.39 [m, 2H, CH_2N], 2.97 [m, 2H, CH_2S], 5.14 [m, 1H, NH]. Anal. Calcd for $C_{40}H_{49}BN_7O_2S_4Zn\cdot 0.5CH_2Cl_2$ ($M_r = 864.34 + 42.47$): C, 53.64; H, 5.56; N, 10.81; S, 14.14; Zn 7.21. Found: C, 53.76; H, 5.40; N, 10.81; S, 14.26; Zn, 7.27.

1f. Like **1a** from 33 mg (31 μL, 0.30 mmol) of thiophenol, 0.11 g (0.30 mmol) of $Zn(ClO_4)\cdot 6H_2O$, and 0.20 g (0.30 mmol) of $KTti^{Xyl}$. Yield 176 mg (73%) of **1f** as colorless crystals, mp 220 °C (dec). ν(BH) 2437 cm^{-1}. ^1H NMR ($CDCl_3$): 6.77 [d, $J = 3.0$ Hz, 2H, Ph(2,6)], 7.13 [m, 3H, Ph(3,4,5)]. Anal. Calcd for $C_{39}H_{39}BN_6S_4Zn$ ($M_r = 796.24$): C, 58.83; H, 4.94; N, 10.55; S, 16.11; Zn, 8.21. Found: C, 57.17; H, 4.90; N, 10.21; S, 15.61; Zn, 7.96.

1g. Like **1d** from 41 mg (40 μL, 0.30 mmol) of 2,6-dimethylthiophenol, 0.11 g (0.30 mmol) of $Zn(ClO_4)\cdot 6H_2O$, and 0.20 g (0.30 mmol) of $KTti^{Xyl}$. Yield 197 mg (79%) of **1g** as colorless crystals, mp 220 °C (dec). ν(BH) 2436 cm^{-1}. ^1H NMR ($CDCl_3$): 2.17 [s, 6H, CH_3], 7.00 [m, 3H, C_6H_3]. Anal. Calcd for $C_{41}H_{43}BN_6S_4Zn\cdot 0.5CH_2Cl_2$ ($M_r = 824.30 + 42.46$): C, 57.13; H, 5.22; N, 9.71; S, 14.81; Zn, 7.55. Found: C, 57.51; H, 5.12; N, 9.70; S, 14.80; Zn, 7.55.

1h. Like **1a** from 46.6 mg (0.30 mmol) of *p*-nitrothiophenol, 0.11 g (0.30 mmol) of $Zn(ClO_4)\cdot 6H_2O$, and 0.20 g (0.30 mmol) of $KTti^{Xyl}$. Yield 184 mg (74%) of **1h** as yellow crystals, mp 240 °C (dec). ν(BH) 2437 cm^{-1}. ^1H NMR ($CDCl_3$): 7.30 [d, $J = 8.9$ Hz, 2H, Ph(2,6)], 7.61 [d, $J = 8.9$ Hz, 2H, Ph(3,5)]. Anal. Calcd for $C_{39}H_{38}BN_7O_2S_4Zn$ ($M_r = 841.24$): C, 55.68; H, 4.55; N, 11.66; S, 15.25; Zn, 7.77. Found: C, 55.51; H, 4.55; N, 11.69; S, 15.36; Zn, 7.83.

1i. A solution of 112 mg (0.72 mmol) of *p*-nitrothiophenol in 40 mL of methanol was deprotonated by adding 0.6 mmol of the NaOMe solution. To this solution a solution of 0.17 g (0.58 mmol) of $Zn(NO_3)_2\cdot 6H_2O$ in 15 mL of methanol was added dropwise with stirring. Then a solution of 0.28 g (0.58 mmol) of $KTti^{tBu}$ in 50 mL of methanol was added within 15 min, upon which a yellow precipitate was formed. This was filtered off and dried in vacuo, leaving behind 170 mg (42%) of **1i** as a yellow powder, mp 245 °C (dec). ν(BH) 2420 cm^{-1}. ^1H NMR ($CDCl_3$): 7.39 [d, $J = 8.6$ Hz, 2H Ph(2,6)], 7.81 [d, $J = 8.6$ Hz, 2H, Ph(3,5)]. Anal. Calcd for $C_{27}H_{38}BN_7O_2S_4Zn$ ($M_r = 697.11$): C, 46.52; H, 5.49; N, 14.06; S, 18.40. Found: C, 46.37; H, 5.85; N, 14.49; S, 17.99.

1j. Like **1i** from 75 mg (0.48 mmol) of *p*-nitrothiophenol, 0.14 g (0.48 mmol) of $Zn(NO_3)_2\cdot 6H_2O$, and 0.30 g (0.48 mmol) of $KTti^{Tol}$. Yield 198 mg (51%) of **1j** as a yellow powder, mp 195 °C. ν(BH) 2438 cm^{-1}. ^1H NMR ($CDCl_3$): 7.69 [d, $J = 10.4$ Hz, 2H, Ph(2,6)], 8.26 [d, $J = 10.4$ Hz, 2H, Ph(3,5)]. Anal. Calcd for $C_{36}H_{32}BN_7O_2S_4Zn$ ($M_r = 799.16$): C, 54.11; H, 4.04; N, 12.27; S, 16.05. Found: C, 53.36; H, 4.16; N, 12.09; S, 15.57.

1k. Like **1i** from 112 mg (0.72 mmol) of *p*-nitrothiophenol, 0.17 g (0.58 mmol) of $Zn(NO_3)_2\cdot 6H_2O$, and 0.40 g (0.58 mmol) of $KTti^{Cum}$. Yield 220 mg (35%) of **1k** as a yellow powder, mp 225 °C (dec). ν(BH) 2427 cm^{-1}. ^1H NMR ($CDCl_3$): 7.15−7.38 [m, 14H, Cum + nitrophenyl], 7.61 [d, $J = 9.0$ Hz, 2H, Ph(3,5)]. Anal. Calcd for $C_{42}H_{44}BN_7O_2S_4Zn$ ($M_r = 883.32$): C, 57.11; H, 5.02; N, 11.10; S, 14.52. Found: C, 57.44; H, 5.25; N, 11.12; S, 14.47.

1l. Like **1d** from 60 mg (40 μL, 0.30 mmol) of pentafluorothiophenol, 0.11 g (0.30 mmol) of $Zn(ClO_4)_2\cdot 6H_2O$, and 0.20 g (0.30 mmol) of $KTti^{Xyl}$. Yield 204 mg (70%) of **1l** as colorless crystals, mp 230 °C (dec). ν(BH) 2440 cm^{-1}. ^{19}F NMR ($CDCl_3$) −138.5, −169.6 and −177.0 ppm. Anal. Calcd for $C_{39}H_{34}BF_5N_6S_4Zn$ ($M_r = 886.19$): C, 52.86; H, 3.87; N, 9.48; S, 14.47; Zn, 7.38. Found: C, 52.63; H, 3.94; N, 9.33; S, 14.33; Zn, 7.31.

2a. A solution of 19 mg (22.2 μL, 0.30 mmol) of ethanethiol in 10 mL of methanol was deprotonated by adding 0.30 mmol of the NaOMe solution. This solution was added dropwise with stirring within 30 min to a solution of 0.11 g (0.30 mmol) of $Zn(ClO_4\cdot 6H_2O$ and 0.20 g (0.30 mmol) of $KTti^{Xil}$ in 30 mL of methanol. After stirring for 24 h all volatiles were removed in vacuo at 40 °C. The residue was extracted with 20 mL of dichloromethane, filtered, and evaporated to dryness again. Crystallization from methanol/dichloromethane (3:1) yielded 170 mg (73%) of **2a** as colorless crystals, mp 260 °C (dec). ν(BH) 2423, $\nu(ClO_4)$ 1095 cm^{-1}. ^1H NMR ($CDCl_3$): 0.66 [t, $J = 7.4$ Hz, 3H, CH_3(Et)], 2.09 [q, $J = 7.4$ Hz, 2H, CH_2(Et)]. Anal. Calcd for $C_{68}H_{73}B_2ClN_{12}O_4S_7Zn_2$ ($M_r = 1533.17$): C, 53.22; H, 4.79; N, 10.95; S, 14.63; Zn, 8.52. Found: C, 52.45; H, 4.90; N, 10.72; S, 14.58; Zn, 8.49.

2b. The reaction resulting in **2b** is described here, despite the poor identification of the complex, because it was the structure determination of **2b** that made us aware of the existence of complexes **2**.

A solution of 0.25 g (0.39 mmol) of $Tti^{tBu}Zn-OClO_3$[12] in 10 mL of methanol was treated with 10 mL of ethanethiol and brought to reflux shortly. After filtration the solution was kept in a refrigerator. After one week a few crystals of **2b** had separated which were used for the spectra and the structure determination. ν(BH) 2424, $\nu(ClO_4)$ 1099 cm^{-1}. ^1H NMR ($CDCl_3$): 0.83 [t, $J = 7.5$ Hz, 3H, CH_3(Et)], 2.50 [q, $J = 7.5$ Hz, 2H, CH_2(Et)]. Several variations of this preparation led neither to a higher yield of **2b** nor to the formation of the desired $Tti^{tBu}Zn-SC_2H_5$.

3a. A solution of 17 mg (0.30 mmol) of KOH in 5 mL of methanol was added dropwise with stirring to a solution of 0.16 g (0.30 mmol) of $Tti^{Xyl}Zn-OClO_3$[13] in 10 mL of methanol, while a slow stream of H_2S was passed through the solution. After saturating with H_2S for 30 min the solution was stirred for 15 h. After filtration the filtrate was evaporated to dryness, and the residue was dissolved in 10 mL of dichloromethane, filtered, and evaporated to dryness again. Crystallization from methanol/dichloromethane (3:1) yielded 109 mg (66%) of **3a** as colorless crystals, mp 198 °C (dec). ν(BH) 2435 cm^{-1}. ^1H NMR ($CDCl_3$): −1.69 [s, 1H, SH]. Anal. Calcd for $C_{33}H_{35}BN_6S_4Zn\cdot 3CH_3OH$ ($M_r = 720.14 + 96.13$): C, 52.97; H, 5.80; N, 10.30; S, 15.71; Zn, 8.01. Found: C, 53.74; H, 5.22; N, 9.96; S, 14.85; Zn, 7.57.

Reactions with Methyl Iodide. Methyl iodide was applied as a 1 M solution in chloroform. About 0.05 mmol of the thiolate complex **1** was dissolved in 5 mL of chloroform and treated with the 4-fold molar amount of the methyl iodide solution. Reactions were followed by ^1H NMR. After completion the solvent was removed in vacuo. The residue was washed with two 2-mL portions of diethyl ether and dried in vacuo. The residue of the reactions of

Table 2. Crystallographic Data

	1a	**1c**	**1e**	**1f**	**1h**	**1k**
formula	$C_{35}H_{39}BN_6S_4Zn \cdot 3CH_3OH$	$C_{40}H_{41}BN_6S_4Zn \cdot 2CH_3CN$	$C_{40}H_{49}BN_7O_2S_4Zn \cdot CH_3OH$	$C_{78}H_{78}B_2N_{12}S_8Zn_2 \cdot 3CH_3OH$	$C_{39}H_{38}BN_7O_2S_4Zn$	$C_{42}H_{44}BN_7O_2S_4Zn \cdot CH_3CN$
MW	844.3	892.3	895.3	1688.6	841.2	924.3
space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
Z	8	2	2	2	4	2
a (Å)	13.335(2)	9.60(1)	9.439(2)	26.490(5)	9.779(2)	12.523(1)
b (Å)	17.244(3)	14.80(2)	15.564(3)	12.210(3)	32.709(6)	14.243(1)
c (Å)	36.902(5)	17.02(2)	16.234(3)	34.559(5)	13.584(2)	15.534(1)
α (deg)	90	74.16(2)	75.993(4)	90	90	107.608(2)
β (deg)	90	78.86(2)	83.827(4)	130.062(9)	102.445(7)	104.358(2)
γ (deg)	90	76.81(2)	80.030(4)	90	90	109.185(2)
V (Å^3)	8486(2)	2242(5)	2273.8(7)	8555(3)	4243(1)	2301.6(4)
d (calc) [g cm^{-3}]	1.32	1.32	1.31	1.31	1.32	1.33
μ (Mo Kα) [mm^{-1}]	0.82	0.78	0.77	0.81	0.82	0.76
*R*1 (obs. reflns)	0.046	0.107	0.065	0.065	0.052	0.071
w*R*2 (all reflns)	0.137	0.294	0.199	0.212	0.175	0.243

	1l	**2a**	**2b**	**3a**	**5**
formula	$C_{39}H_{34}BF_5N_6S_4Zn \cdot CH_2Cl_2$	$C_{68}H_{73}B_2ClN_{12}O_4S_7Zn_2 \cdot 0.5CH_3OH$	$C_{44}H_{73}B_2ClN_{12}O_4S_7Zn_2$	$C_{33}H_{35}BN_6S_4Zn \cdot CH_3OH$	$C_{35}H_{40}BN_6O_4PS_3Zn \cdot 4CH_3OH$
MW	971.1	1550.74	1246.4	752.1	940.3
space group	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$P2(1)2(1)2(1)$	$P2(1)/c$
Z	4	4	2	4	4
a (Å)	12.555(2)	16.999(5)	10.865(3)	10.731(3)	11.185(2)
b (Å)	19.139(3)	20.114(6)	17.411(5)	11.493(3)	17.701(3)
c (Å)	19.160(3)	23.796(7)	17.756(5)	28.977(7)	23.210(4)
α (deg)	90	90	92.114(5)	90	90
β (deg)	98.856(3)	106.376(7)	101.344(5)	90	98.895(3)
γ (deg)	90	90	91.189(5)	90	90
V (Å^3)	4549(1)	7806(4)	3290(2)	3573(1)	4540(1)
d (calc) [g cm^{-3}]	1.42	1.32	1.26	1.39	1.37
μ (Mo Kα) [mm^{-1}]	0.89	0.89	1.04	0.96	0.77
*R*1 (obs. reflns)	0.089	0.095	0.145	0.046	0.077
w*R*2 (all reflns)	0.318	0.355	0.452	0.151	0.281

1a, **c**, **d**, **e**, **f**, and **h** was spectroscopically pure Tti^{xyl}ZnI.[13] The resulting methylthioethers were detected by ^{1}H NMR in the reaction solutions and were contained in the diethyl ether extracts (except $CH_3SC_2H_5$). Their identification rests on their reported ^{1}H NMR data.[2] The reaction of **1j** with CH_3I according to eq 2 was only performed in the manner of the kinetic investigation (see below).

From **1a** (32 mg, 0.043 mmol) resulted 33 mg (94%) of Tti^{Xyl}ZnI (**6**).

From **1c** (41 mg, 0.051 mmol) resulted 37 mg (90%) of **6**.

From **1d** (48 mg, 0.054 mmol) resulted 26 mg (58%) of **6**.

From **1e** (24 mg, 0.028 mmol) resulted 19 mg (85%) of **6**.

From **1f** (37 mg, 0.047 mmol) resulted 31 mg (82%) of **6**.

From **1h** (38 mg, 0.045 mmol) resulted 25 mg (67%) of **6**.

Kinetic Measurements. The standard solutions of complexes **1h** and **1j** and of methyl iodide in $CDCl_3$ (99.8%) 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 concentration of **1h** was adjusted to 0.010 M for all five measurements and to 0.10, 0.15, 0.20, 0.25, and 0.30 M for CH_3I, respectively. The concentration of **1j** was adjusted to 0.005 M for all six measurements and to 0.020, 0.030, 0.035, 0.045, 0.055, and 0.070 M for CH_3I, respectively. In case of **1h** the low-field aromatic NMR signal of the *p*-nitrothiophenolate group in the complex and in the resulting thioether was used for intensity recording. In case of **1j** the intensity of the methyl resonance of the thioether was recorded. Data were averaged for four runs with **1h** and for two runs with **1j**, being reproducible within ±10%. The calculations yielded k_{obs} values of 1.08-, 1.67-, 3.91-, 4.19-, and 5.40 × 10^{-4} s^{-1} for **1h** and of 1.9-, 2.8-, 3.2-, 4.1-, 4.9-, and 6.2 × 10^{-4} s^{-1} for **1j**, respectively.

Reaction of 1a with Trimethyl Phosphate. A solution of 44 mg (0.059 mmol) of **1a** and 6.9 μL (8.2 mg, 0.059 mmol) of trimethyl phosphate in 10 mL of chloroform was kept at 40 °C for five weeks. According to ^{1}H NMR the only reaction products were $CH_3SC_2H_5$ and Tti^{Xyl}ZnI, and the reaction was 75% complete after this time. All volatiles were removed in vacuo, and the residue was extracted with 10 mL of dichloromethane, filtered, and evaporated to dryness again. Crystallization from methanol/dichloromethane (3:1) yielded 16 mg (33%) of **5** as colorless crystals, mp 192 °C. *ν*(BH) 2443 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.31 (d, J = 12.0 Hz, 6H, OMe). ^{31}P NMR ($CDCl_3$): −10.6. Anal. Calcd for $C_{35}H_{40}BN_6O_4PS_3Zn$ (M_r = 812.11): C, 51.76; H, 4.96; N, 10.35; S, 11.85; Zn, 8.05. Found: C, 51.06; H, 5.07; N, 10.13; S, 11.90; Zn, 8.09.

Independent Preparation of Complex 5. A solution of 38 mg (0.30 mmol) of dimethylphosphoric acid in 10 mL of methanol

was deprotonated by adding 0.30 mmol of the NeOMe solution. This solution was added dropwise with stirring to a solution of 0.11 g (0.30 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ and 0.20 g (0.30 mmol) of $KTti^{Xyl}$ in 20 mL of methanol. After stirring for 24 h all volatiles were removed in vacuo at 40 °C. The residue was extracted with 20 mL of dichloromethane, filtered, and evaporated to dryness again. Crystallization from methanol/dichloromethane (3:1) yielded 168 mg (68%) of **5** as colorless crystals.

Reconversion of 5 to 1a. A solution of 28 μL (24 mg, 0.38 mmol) of ethanethiol in 15 mL of methanol was deprotonated with 1.5 mL (0.38 mmol) of the NaOMe stock solution. This solution was added slowly and dropwise to a solution of 0.18 g (0.22 mmol) of **5** in 45 mL of methanol. After stirring for 12 h all volatiles were removed in vacuo, and the residue was extracted with 10 mL of dichloromethane, filtered, and evaporated to dryness again. A total of 129 mg (78%) of spectroscopically pure **1a** remained as a colorless powder.

Structure Determinations. Crystals of **1c** and **1k** were obtained by recrystallization from acetonitrile; all others were taken as obtained from the workup procedures. Data sets were obtained at 240 K with a Bruker AXS Smart CCD diffractometer and subjected to empirical absorption corrections (SADABS). The structures were solved with direct methods and refined anisotropically using the SHELX program suite.[26] 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.[27] Table 2 lists the crystallographic details.

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Supporting Information Available: Fully labeled ORTEP plots and X-ray crystallographic files in CIF format for the 11 structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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