Zinc Thiolate Complexes of (N,N,S)-Tridentate Ligands for the Modeling of Thiolate Alkylating Enzymes

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Zinc thiolate complexes of three tridentate (N,N,S) ligands were prepared as models for the structure and function of thiolate alkylating zinc enzymes. *N*-(2-Mercaptoisobutyl)(2-pyridin-2-yl-methyl)amine (**L^1**) forms isobutylthiolate-bridged dinuclear complexes with ZnN_2S_3 coordination. *N*-(2-Mercaptoisobutyl)(2-pyridin-2-yl-ethyl)amine (**L^2**) yields isobutylthiolate-bridged dinuclear complexes in which the pyridine donor is not coordinated to zinc, resulting in a $ZnNS_3$ coordination. Only *N*-(2-mercaptoisobutyl)(2-pyridin-2-yl-ethyl)methylamine (**L^3**) forms the desired mononuclear complexes with ZnN_2S_2 coordination. The latter react with the alkylating agents CH_3I and $PO(OCH_3)_3$ in a two-step process. In the first step the isobutylthiolate function is methylated and its position in the ligand sphere of zinc is taken by I^- or $OPO(OCH_3)_2^-$, respectively, and in the second step the additional thiolate ligand is methylated and replaced by a second iodide or dimethyl phosphate anion.

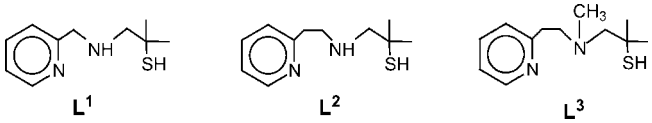
Introduction

In recent years a number of thiolate alkylating enzymes have been identified that contain zinc in their active centers,[1] the most prominent of which is cobalamine-independent methionine synthase.[2] An unusual feature of these enzymes is that they contain zinc in a sulfur-rich ligand environment, which can typically be represented as NS_2ZnX or N_2SZnX, where N and S stand for the side-chains of histidine and cysteine and X is the coordination position of the substrate. It is believed that the thiol substrates, for example homocysteine, are attached to zinc as thioalates prior to alkylation, for example to methionine. An open mechanistic question is whether the alkylation, typically a methylation by methyl tetrahydrofolate, takes place at the zinc-bound or at the free thiolate.

We[3–5] and others[6–11] have attempted to reproduce this biological process with zinc thiolate complexes of various polydentate ligands, using methyl iodide, dimethyl sulfate, or trimethyl phosphate as methylating agents. In most cases the coligands were bidentate chelators or tripodal donors offering only N coordination. In those cases where mechanistic studies were performed it was found that the thiolate is alkylated in the zinc-bound state. Thus, a reasonable approximation to a functional modeling of the enzymes has been achieved, albeit with rather low reaction rates and not in a catalytic fashion.

At this point the major challenges concern a better structural modeling of the enzymes, which may also be a way to achieve higher reactivities of the zinc thiolate model complexes. This requires modeling the protein environment of zinc by tridentate or tripodal ligands with N_2S and NS_2 donor sets, of which N is part of a nitrogen heterocycle representing histidine's imidazole and S is a thiolate sulfur representing cysteine's thiolate. We are not aware of a model study employing such an NS_2 ligand, and so far just one type of such N_2S ligands seems to have been used for thiolate alkylation in zinc complexes.[8,9]

We have reported various tridentate N_2S ligands[12–15] as well as pyrazolylborate-derived NS_2[16] and N_2S tripods.[17] While we have previously focused on modeling hydrolytic enzymes or alcohol dehydrogenase with their zinc complexes, we are at present using their zinc thiolate complexes for studies of thiolate alkylation. This paper reports our results with the tridentate N_2S systems **L^1**–**L^3**. The goal of our study was to find out whether mononuclear tetrahedral **L**·Zn–SR complexes of **L^1**–**L^3** are accessible and how they behave toward alkylating reagents.



Results and Discussion

All three ligands in their free form are aliphatic thiols and by design are good chelators. They are disubstituted at

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the α-carbon of the thiolate function with the purpose of introducing some steric strain in order to reduce their tendency to bridge. Their synthesis consists in the ring opening of 2,2-dimethylthiirane by the corresponding pyridine-substituted aliphatic amine. The two methyl substituents and the CH_2 group of their mercaptoethylamine functions make it easy to identify the complexes of **L¹**–**L³** by ^{1}H NMR spectroscopy. The zinc thiolate complexes of **L¹**–**L³** could be expected to have a ZnN_2S_2 coordination, which in almost all cases − in coordination compounds as well as in zinc-containing proteins − was found to imply mononuclear species with a tetrahedral coordination of zinc.

N-(2-Mercaptoisobutyl)(2-pyridin-2-ylmethyl)amine (L¹)

Ligand **L¹** and some of its zinc complexes have been described previously by us.[14] We observed that the isobutylthiolate function of **L¹** has a high bridging tendency and that the zinc ions in the resulting oligonuclear complexes have coordination numbers of 5 or 6. Yet, except for the thiolate sulfur only hard donor atoms (N and O) are present in these complexes and the N_2S_2 donor composition has not been tested.

This was done now. The thiophenolate complex **1** was generated in a one-step synthesis from deprotonated **L¹**, zinc nitrate, and potassium thiophenolate. The NMR spectroscopic data of **1** are inconclusive in terms of composition and structure in solution, but in the crystalline state **1** was found to be dimeric with a ZnN_2S_3 coordination.

L¹•Zn-SC$_6$H$_5$
1

Figure 1 shows the centrosymmetrical dinuclear molecular units of **1** in which the isobutylthiolate groups function as bridging ligands as observed before.[14] The perfectly planar central Zn_2S_2 unit of the complex is close to being a square. The coordination of the zinc ions is roughly trigonal bipyramidal (85% TBP according to the dihedral angle method of Holmes[18]). This is not so evident from the S1–Zn–N1 angle of 159°, but clearly so from the fact that the axial bonds Zn–S1 and Zn–N1 are considerably longer than their equatorial counterparts Zn–S1′, Zn–S2, and Zn–N2. Complex **1** therefore closely resembles the **L¹**·Zn-acetate complex.[14]

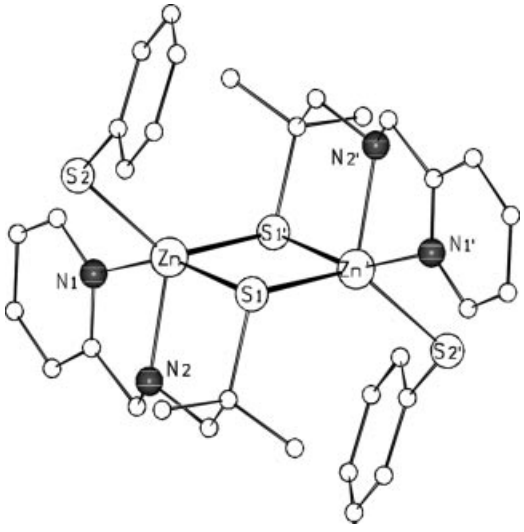


Figure 1. Structure of **1** in the solid state. Relevant bond lengths [Å]: Zn–S1 2.514(2), Zn–S1′ 2.370(2), Zn–S2 2.321(2), Zn–N1 2.305(4), Zn–N2 2.134(4).

One reason for the inaccessibility of tetrahedral zinc complexes with ligand **L¹** seems to be the fact that, upon complexation with **L¹**, two five-membered chelate rings are formed. These enforce two small bond angles and therefore encourage trigonal bipyramidal or octahedral coordination despite the high sulfur content in the ligand sphere of the metal. The investigations with ligand **L¹** were therefore abandoned in favor of those with **L²** and **L³**.

N-(2-Mercaptoisobutyl)(2-pyridin-2-ylethyl)amine (L²)

This ligand has not been described before. We now found that it is easily accessible from 2,2-dimethylthiirane and 2-(2-aminoethyl)pyridine as a colorless liquid with typical ^{1}H NMR resonances for its aliphatic constituents.

While we found it difficult to obtain zinc alkanethiolate complexes of **L²**, aromatic thiolates could easily be incorporated. Again, they resulted from a one-pot synthesis using deprotonated **L²**, $Zn(NO_3)_2$, and the corresponding thiolate. Complexes **2a**–**d** were obtained in reasonable yields as colorless, crystalline materials, except for yellow **2c**.

L²•Zn-SAr

	2a	**2b**	**2c**	**2d**
Ar	C$_6$H$_5$	*p*-CH$_3$C$_6$H$_4$	*p*-NO$_2$C$_6$H$_4$	C$_6$F$_5$

The spectroscopic data of all four complexes **2** are similar enough to justify the statement that they all have a structure like the one that was determined for **2a** (see Figure 2). Again, the complexes crystallize as centrosymmetrical dimers with bridging isobutylthiolate functions.

The unusual feature of this structure is the noncoordination of the pyridine donor of **L²**. Thus, while the expected coordination number 4 is achieved for zinc, this is not due to the lengthening of the ligand arm between the two nitrogen donors but due to the fact that thiolate bridging is preferred over pyridine coordination. Therefore, with three thiolate ligands bound to zinc, anything but a tetrahedral coordination is unlikely, and the $ZnNS_3$ coordination pattern ensues. The coordination geometry of zinc is extremely distorted tetrahedral. The two smallest bond angles (S1–Zn–S1′ and S1–Zn–N2) are enforced by the Zn_2S_2 diamond and the chelate ring, respectively. The opening in the ligand sphere resulting from this then allows the very large S1–

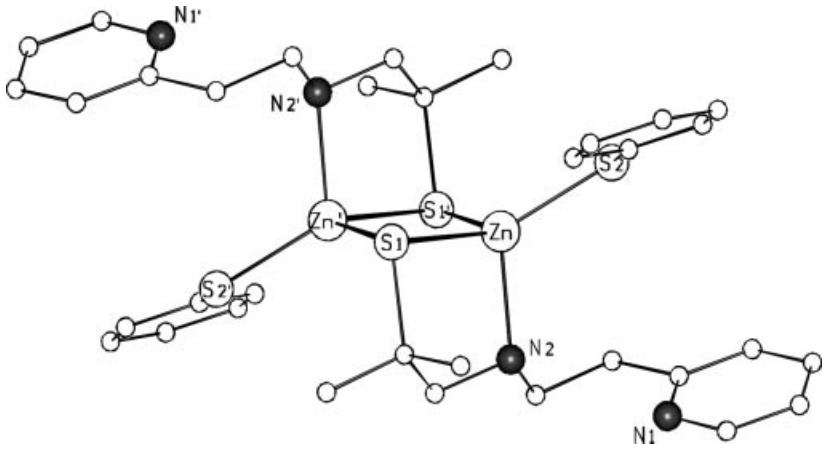


Figure 2. Structure of **2a** in the solid state. Relevant bond lengths [Å] and angles [°]: Zn–S1 2.375(4), Zn–S1′ 2.377(4), Zn–S2 2.254(3), Zn–N2 2.101(5); S1–Zn–S1′ 99.3(1), Zn–S1–Zn′ 80.7(1), S1–Zn–N2 90.1(1), S1–Zn–S2 130.0(1).

Zn–S2 angle. Neither of the structural features of **2a** is unprecedented. A similar dimeric structure with severe bond-angle deviations has been described by Kellogg for an NS_2 chelate ligand,[19] and we have observed the noncoordination of the pyridine arm in the ZnL_2 complex of $\mathbf{L^1}$.[17]

N-(2-Mercaptoisobutyl)(2-pyridin-2-ylethyl)methylamine ($\mathbf{L^3}$)

While ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ yielded zinc complexes that are not suitable for the intended thiolate alkylation studies, ligand $\mathbf{L^3}$, which differs from $\mathbf{L^2}$ only by the methyl group on the central nitrogen atom, did allow the formation of mononuclear tetrahedral **L**·Zn–SR complexes. $\mathbf{L^3}$ was first described by Goldberg et al. and used for zinc chemistry unrelated to thiolate alkylation,[20–22] and these authors had already noted that the larger chelate ring size in relation to that provided by ligands like $\mathbf{L^1}$ favors the formation of four-coordinate complexes.[21] We verified the ability of $\mathbf{L^3}$ to form tetrahedral **L**·Zn–X complexes with soft donors X by preparing $\mathbf{L^3}$·ZnCl from zinc chloride. The molecular structure of $\mathbf{L^3}$·ZnCl (Figure 3) shows that in the mononuclear complexes of these ligands the tetrahedral coordination is also severely distorted due to the small bond angles between the chelate donors and, subsequently, the large bond angle between the two soft donors Cl and S.

$\mathbf{L^3}$•Zn-SR

	3a	**3b**	**3c**
R	CH_2CF_3	$CH_2C_6H_5$	$CH_2C_6H_4Cl$
	3d	**3e**	**3f**
R	C_6H_5	*p*-$NO_2C_6H_4$	C_6F_5

Just like $\mathbf{L^2}$, ligand $\mathbf{L^3}$ did not facilitate access to simple zinc alkanethiolate complexes. However, the trifluoroe-

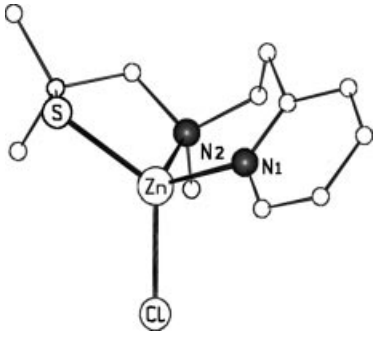


Figure 3. Structure of $\mathbf{L^3}$·Zn–Cl. Relevant bond lengths [Å] and angles [°]: Zn–Cl 2.2354(5), Zn–S 2.2532(5), Zn–N1 2.057(1), Zn–N2 2.108(1); N1–Zn–N2 98.96(5), S–Zn–N2 92.72(4), Cl–Zn–N2 116.38(4), S–Zn–N1 120.09(4), Cl–Zn–N1 101.66(4), Cl–Zn–S 124.55(2).

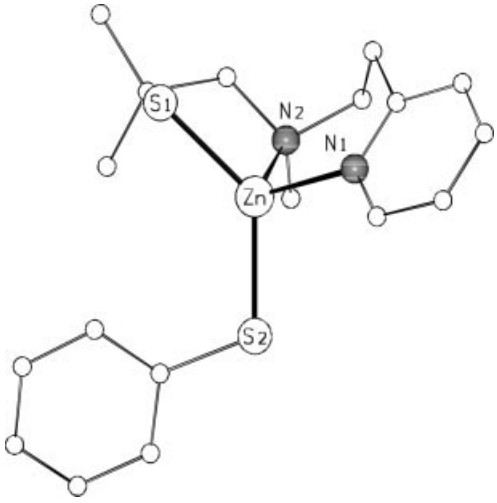
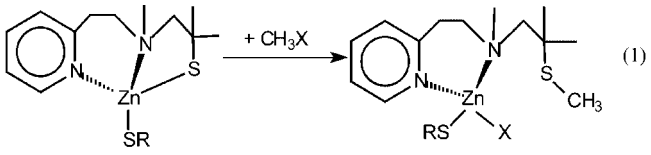


Figure 4. Molecular structure of $\mathbf{L^3}$·Zn–SC_6H_5 (**3d**). Relevant bond lengths [Å] and angles [°]: Zn–N1 2.076(7), Zn–N2 2.149(9), Zn–S1 2.273(3), Zn–S2 2.277(3); N1–Zn–N2 96.9(3), N1–Zn–S1 113.1(2), N1–Zn–S2 102.3(2), N2–Zn–S1 90.8(2), N2–Zn–S2 116.0(2), S1–Zn–S2 132.4(1).

thanethiolate complex **3a**, the benzylthiolate complexes **3b** and **3c**, as well as the arenethiolate complexes **3d–f** could be synthesized from L^3·ZnBr[21] and the corresponding thiolates. Complexes **3a–f** were isolated in good yields. Except for yellow **3e** they form colorless crystals.

The structures of **3d**, **3e**, and **3f** were determined. They are very similar, making it sufficient to discuss that of **3d**. As Figure 4 shows, the ZnN_2S_2 coordination pattern in the thiolates very much resembles the ZnN_2SCl coordination pattern in the chloride (see Figure 3): the bond angles for the two chelate rings are far below the tetrahedral angle, and the S–Zn–S angle is far above it. Complex **3d** shares these features with our (N_2S-chelate)Zn–SR complex derived from the N_2S-chelate ligand MPPA.[13] The Zn–N and Zn–S distances of the L^3·Zn–SR complexes are in the normal range, comparing well with those both in (N_2S-chelate)[12–14] and in (N_2S-tripod)Zn–SR complexes.[23,24]

The coordination pattern of zinc in complexes **3** is close enough to that in the thiolate alkylating enzymes to justify the investigation of alkylating reactions. They were performed for **3d–f** using methyl iodide and for **3d** using trimethyl phosphate. It was found that both thiolate units attached to zinc are alkylated. However, the alkanethiolate function which is part of ligand L^3 reacts first, according to Equation (1).

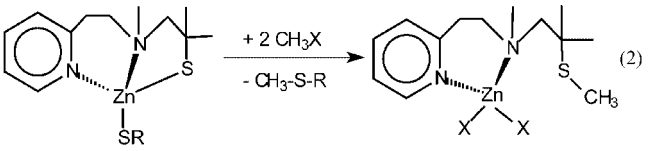


3d: R = C_6H_5
3e: R = $C_6H_4NO_2$
3f: R = C_6F_5

4d: R = C_6H_5, X = I
4e: R = $C_6H_4NO_2$, X = I
4f: R = C_6F_5, X = I
5d: R = C_6H_5, X = $OPO(OMe)_2$

Equimolar amounts of **3d–f** and methyl iodide react smoothly at room temperature in nonpolar solvents. The conversion of ligand L^3 into its methylated form Me-L^3 was evident from the ^{1}H NMR spectra (see Experimental Section), which also indicate by the chemical shifts of the SCH_3 units that in the isolated complexes **4d–f** the thioether functions are not coordinated to zinc, as observed before for a related (N_2S)Zn–SR system and proved by a structure determination.[8] While this could not be proved here by a structure determination it corresponds to the experience that, after alkylation, the sulfur donor is released from zinc and replaced by the anionic constituent of the alkylating agent.[3–5] Actually, the weak donor qualities of thioethers toward zinc, and hence their easy removal from the metal, provide an important part of the driving force for thiolate alkylation by zinc enzymes.[1,2] For complexes **3d–f**, however, the preferred alkylation at the alkanethiolate function corresponds to a partial blocking of ligand L^3, thereby hampering its quality as a model ligand for biomimetic chemistry.

The preference for alkylation at the isobutylthiolate function was not so large as to prevent alkylation at the benzenethiolate function entirely. The NMR spectra of the reaction solutions showed the presence of the aromatic thioethers before the alkylation of the aliphatic thiolate functions was complete. In accord with this the use of a large excess of the alkylating agent brought the reactions to completion according to Equation (2) under the same reaction conditions as for Equation (1).



3d: R = C_6H_5
3e: R = $C_6H_4NO_2$
3f: R = C_6F_5

6: X = I
7: X = $OPO(OMe)_2$

The aromatic thioethers ($CH_3SC_6H_5$ from **3d**, $CH_3SC_6H_4$-*p*-NO_2 from **3e**, $CH_3SC_6F_5$ from **3f**) were isolated and identified from their ^{1}H NMR spectra. The product complexes **6** and **7** bearing the partially blocked ligand Me-L^3 offer no special features; they have the conventional ZnN_2Hal_2 and ZnN_2O_2 compositions. The assumption that the thioether function in these complexes is not coordinated to zinc is backed by the fact that there is not a single structure of a complex of ZnN_2Hal_2 coordination known which has any other donor coordinated to zinc.

The alkylation of **3d** with trimethyl phosphate was included in this investigation to test the ability of complexes **3** to model the function of the Ada protein, a zinc enzyme that repairs damaged DNA by transferring alkyl groups from its phosphate units to thiolates.[1,25] Yet, as observed before,[1,5] trimethyl phosphate is so much less reactive than methyl iodide that rather forcing reaction conditions had to be applied for the alkylation process. While the reactions with CH_3I proceeded smoothly in chloroform at room temperature, for the $PO(OMe)_3$ reactions the reagents had to be heated to 80 °C in DMSO for 10–20 days before the formation of **5d** or **7** was complete, and the products could not be isolated pure due to partial decomposition. This supports the notion that alkylations by trimethyl phosphate and by methyl iodide occur by different mechanisms. The facile alkylation by methyl iodide in nonpolar media, and mechanistic evidence from kinetic data,[3–5] support the assumption that it occurs as an intramolecular process at the zinc-bound thiolates. The forcing conditions and the polar environment needed for alkylation by trimethyl phosphate, as well as mechanistic information from related alkylations of $Zn(SR_4)^{2-}$ species by trimethyl phosphate in very polar solvents,[26] make it likely that the thiolates dissociate from zinc before they react.

Conclusions

In our series of investigations on the modeling of thiolate alkylating enzymes by zinc complexes the ligands L^1–L^3

provide a coordination environment for zinc which more closely than before resembles that in the enzymes. While the studies have shown that **L[1]**–**L[3]** are viable tridentate N_2S donors, they have also made clear that the peculiarities of the coordination chemistry of zinc call for a still better control of the donor arrangement and its functionality around the metal center.

The most striking example of this is the fact that despite their high similarity all three ligands yield zinc thiolate complexes **L**·Zn–SR of completely different structure. Although the ZnN_2S_3 pattern in **1**, the $ZnNS_3$ pattern in **2**, and the ZnN_2S_2 pattern in **3** can subsequently be explained, they came as a surprise; the prevention of thiolate bridging on going from **2** to **3** simply by attaching a methyl group on the remote side of the coordination sphere is particularly noteworthy. Likewise, the preferred alkylation at the aliphatic thiolate function of ligand **L[3]** rather than the aromatic thiolate functions of the "substrates" SAr is explainable by the simple fact that aliphatic thiolates are more nucleophilic than aromatic ones. Yet it was not predictable, as the chelate effect should have resulted in a reduced reactivity of the intact zinc-bound **L[3]**. This sheds light on the delicate balance of stability and reactivity in the thiolate alkylating zinc enzymes, specifically cobalamine-independent methionine syntheses.[1,2] In this enzyme the substrate to be methylated is homocysteine while the protein fixes zinc by two cysteine residues which obviously are not to be methylated. Certainly model chemistry still needs some efforts to reproduce this.

Experimental Section

General: For general working and measuring procedures, see ref.[27] Organic starting materials were obtained commercially. Ligands **L[1]**[14] and **L[3]**[20] were prepared according to the published procedures.

Ligand L[2]: 2-(2-Aminoethyl)pyridine (1.95 g, 16.0 mmol) and 2,2-dimethylthiirane (1.77 g, 20.0 mmol) were refluxed for 30 h in 30 mL of toluene. After cooling to room temp. and filtration the solvent was removed in vacuo and the residue distilled to give 1.08 g (32%) of **L[2]** as a colorless liquid, b.p. 89–90 °C/10^{-1} mbar. $C_{11}H_{18}N_2S$ (210.34): calcd. C 62.81, H 8.63, N 13.32; found C 62.87, H 8.52, N 13.74. IR (film): $\tilde{\nu}$ = 1587 s, 1568 s cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 1.39 (s, 6 H, CH_3), 1.74 (s, 1 H, SH), 2.70 (s, 2 H, CH_2), 2.98–3.18 (m, 4 H, CH_2), 7.13–7.22 (m, 2 H, Ar), 7.64 (m, 1 H, Ar), 8.58 (d, J = 3.8 Hz, 1 H, Ar) ppm.

1: A solution of $Zn(NO_3)_2·6H_2O$ (0.440 g, 1.48 mmol) in 50 mL of methanol was added dropwise, with stirring, within 2 h to a solution of **HL[1]** (0.291 g, 1.48 mmol) and 1.48 mmol of $KOCH_3$ in 50 mL of methanol. Then, a solution of KSC_6H_5 (0.219 g, 1.48 mmol) in 50 mL of methanol was added and the mixture stirred for 15 h. The solvent was removed in vacuo, the residue was taken up in 40 mL of chloroform, and filtered. The solvent was removed in vacuo again and the residue crystallized from chloroform/hexane (1:1) to give 0.35 g (64%) of **1** as off-white crystals, m.p. 198 °C. $C_{16}H_{20}N_2S_2Zn·CHCl_3$ (369.87 + 119.38): calcd. C 41.73, H 4.33, N 5.73, S 13.11; found C 43.15, H 4.58, N 7.30, S 12.60. IR (KBr): $\tilde{\nu}$ = 1604 s, 1575 s cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 1.28 (br. s, 6 H, CH_3), 2.18 (br. s, 1 H, CH_2), 2.78 (br. s, 1 H, CH_2), 3.91 (br. s, 1 H, CH_2), 4.06 (br. s, 1 H, CH_2), 6.76–6.91 (m, 3 H, Ar), 7.14–7.36 (m, 5 H, Ar), 7.71 (m, 1 H, Ar), 8.36 (br. s, 1 H, Ar) ppm.

2a: A solution of $Zn(NO_3)_2·4H_2O$ (0.447 g, 1.71 mmol) in 40 mL of methanol was added dropwise, with stirring, over a period of 1 h to a solution of **HL[2]** (0.360 g, 1.71 mmol) and 1.71 mmol of $NaOCH_3$ in 50 mL of methanol. Then, a solution of KSC_6H_5 (0.254 g, 1.71 mmol) in 40 mL of methanol was added and the mixture stirred for 15 h. The solvent was removed in vacuo and the residue taken up in 30 mL of chloroform and filtered. The solvent was then removed in vacuo again and the product crystallized from chloroform/hexane (1:1) to give 0.312 g (48%) of **2a** as colorless crystals, m.p. 191 °C. IR (KBr): $\tilde{\nu}$ = 1594 s, 1577 s cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 1.09 (br. s, 3 H, CH_3), 1.41 (br. s, 3 H, CH_3), 2.51–3.06 (br. m, 6 H, CH_2), 6.77–6.91 (m, 3 H, Ar), 7.11 (t, J = 7.4 Hz, 2 H, Ph), 7.20–7.29 (m, 2 H, Ar), 7.58 (m, 1 H, Ar), 8.33 (br. s, 1 H, Ar) ppm.

2b: Like **2a** from $Zn(NO_3)_2·4H_2O$ (0.307 g, 1.17 mmol), **HL[2]** (0.247 g, 1.17 mmol), and HSC_6H_4-*p*-CH_3 (0.145 g, 1.17 mmol). Yield 0.246 g (53%) of **2b** as colorless crystals, m.p. 191 °C. $C_{18}H_{24}N_2S_2Zn$ (397.92): calcd. C 54.33, H 6.08, N 7.04, S 16.12; found C 53.94, H 6.01, N 7.34, S 16.00. IR (KBr): $\tilde{\nu}$ = 1594 s, 1567 m cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 1.12 (br. s, 3 H, CH_3), 1.40 (br. s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.42–3.05 (m, 6 H, CH_2), 6.67 (d, J = 7.8 Hz, 2 H, Ar), 7.07–7.17 (m, 4 H, Ar), 7.59 (m, 1 H, Ar), 8.35 (s, 1 H, Ar) ppm.

2c: Like **2a** from $Zn(NO_3)_2·4H_2O$ (0.468 g, 1.79 mmol), **HL[2]** (0.377 g, 1.79 mmol), and HSC_6H_4-*p*-NO_2 (0.346 g, 1.79 mmol). Yield 0.353 g (46%) of **2c** as colorless crystals, m.p. 182 °C. $C_{17}H_{21}N_3O_2S_2Zn$ (428.89): calcd. C 47.61, H 4.93, N 9.80, S 14.95; found C 47.52, H 4.98, N 9.78, S 14.87. IR (KBr): $\tilde{\nu}$ = 1570 s cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 1.28 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 2.54–3.20 (m, 6 H, CH_2), 7.11–7.18 (m, 2 H, Ar), 7.45 (d, J = 8.6 Hz, 2 H, Ar), 7.56–7.73 (m, 3 H, Ar), 8.34 (br. s, 1 H, Ar) ppm.

2d: Like **2a** from $Zn(NO_3)_2·4H_2O$ (0.439 g, 1.68 mmol), **HL[2]** (0.353 g, 1.68 mmol), and HSC_6F_5 (0.336 g, 1.68 mmol). Yield 0.358 g (45%) of **2d** as colorless crystals, m.p. 206 °C. $C_{17}H_{17}F_5N_2S_2Zn$ (473.85): calcd. C 43.09, H 3.62, N 5.91, S 13.53; found C 43.04, H 3.48, N 6.04, S 13.53. IR (KBr): $\tilde{\nu}$ = 1598 s, 1570 s cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 1.29 (br. s, 3 H, CH_3), 1.40 (br. s, 3 H, CH_3), 2.53–3.33 (m, 6 H, CH_2), 4.73 (br. s, 1 H, NH), 7.20–7.27 (m, 2 H, Ar), 7.71 (t, J = 7.6 Hz, 1 H, Ar), 8.49 (d, J = 4.6 Hz, 1 H, Ar) ppm. ^{19}F NMR ($CDCl_3$): δ = –134.0 (s, 2 F), –163.2 (s, 1 F), –165.1 (s, 2 F) ppm.

L[3]·ZnCl: A solution of **HL[3]** (0.122 g, 3.04 mmol) in 15 mL of methanol was treated dropwise with stirring first with NaOH (0.122 g, 3.04 mmol) in 5 mL of methanol and then with $ZnCl_2$ (0.414 g, 3.04 mmol) in 5 mL of methanol. The mixture was stirred for 20 h, filtered, and the filtrate evaporated to dryness. Recrystallization of the residue from methanol yielded 0.374 g (38%) of **L[3]**·ZnCl as colorless crystals, m.p. 203 °C. $C_{12}H_{19}ClN_2S_2Zn$ (324.20): calcd. C 44.46, H 5.91, N 8.64; found C 43.52, H 5.88, N 8.28. IR (KBr): $\tilde{\nu}$ = 1610 s, 1569 s cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 1.42 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 2.55 (d, J = 13.0 Hz, 1 H, CH_2), 2.78 (s, 3 H, NCH_3), 2.87–3.74 (m, 5 H, CH_2), 7.33 (d, J = 7.8 Hz, 1 H, Ar), 7.47 (t, J = 6.5 Hz, 1 H, Ar), 7.88 (m, 1 H, Ar), 8.81 (d, J = 5.0 Hz, 1 H, Ar) ppm.

3a: A solution of $HSCH_2CF_3$ (0.058 g, 0.50 mmol) and 1 mL of a 0.5 M solution of $NaOCH_3$ in methanol (0.50 mmol) in 30 mL of methanol was added dropwise, with stirring, to a solution of

L^3·ZnBr (0.184 g, 0.50 mmol) in 60 mL of methanol. After stirring overnight the solvent was removed in vacuo. The residue was taken up in 30 mL of chloroform and filtered. After removal of the solvent in vacuo the product was recrystallized from methanol to yield 32 mg (16%) of **3a** as colorless crystals, m.p. 125 °C. $C_{14}H_{21}F_3N_2S_2Zn$ (403.85): calcd. C 41.64, H 5.24, N 6.94, S 15.88; found C 41.68, H 4.56, N 6.45, S 15.44. IR (KBr): $\tilde{\nu}$ = 1608 s, 1571 s cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.40 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3), 2.47 (d, J = 13.0 Hz, 1 H, CH_2), 2.77 (s, 3 H, NCH_3), 2.80–3.59 (m, 7 H, CH_2), 7.31 (d, J = 7.8 Hz, 1 H, Ar), 7.45 (t, J = 6.5 Hz, 1 H, Ar), 7.86 (m, 1 H, Ar), 8.87 (d, J = 4.4 Hz, 1 H, Ar) ppm. ^{19}F NMR ($CDCl_3$): δ = –67.29 (s) ppm.

3b: $HSCH_2C_6H_5$ (0.124 g, 1.00 mmol) in 50 mL of methanol was treated with 2.00 mL (1.00 mmol) of a 0.5 M methanol solution of $NaOCH_3$ and then added dropwise, with stirring, to a solution of **L^3·**ZnBr (0.369 g, 1.00 mmol) in 80 mL of methanol. After stirring overnight the solvent was removed in vacuo, the residue taken up in 25 mL of chloroform, and filtered. The filtrate was evaporated to dryness and the product washed with diethyl ether and dried in vacuo. Recrystallization from hexane/chloroform (2:1) yielded 0.239 g (58%) of **3b** as a colorless powder, m.p. 139 °C. $C_{19}H_{26}N_2S_2Zn$ (411.95): calcd. C 55.40, H 6.36, N 6.80, S 15.57; found C 55.14, H 6.20, N 6.67, S 14.74. IR (KBr): $\tilde{\nu}$ = 1607 s, 1568 m cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 2.50 (d, J = 13.0 Hz, 1 H, CH_2), 2.67 (s, 3 H, NCH_3), 2.76–3.50 (m, 5 H, CH_2), 3.87 (m, 2 H, CH_2), 7.07–7.28 (m, 6 H, Ar), 7.42 (t, J = 4.2 Hz, 1 H, Ar), 7.76 (m, 1 H, Ar), 8.31 (d, J = 5.4 Hz, 1 H, Ar) ppm.

3c: Like **3b** from $HSCH_2C_6H_4Cl$ (0.159 g, 1.00 mmol), 1.00 mmol of $NaOCH_3$, and **L^3·**ZnBr (0.369 g, 1.00 mmol). Yield 0.331 g (74%) of **3c** as a colorless powder, m.p. 164 °C. $C_{19}H_{25}N_2S_2ClZn$ (446.39): calcd. C 51.12, H 5.84, N 6.28, S 14.37; found C 51.08, H 5.55, N 6.13, S 13.48. IR (KBr): $\tilde{\nu}$ = 1606 s, 1566 s cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 2.51 (d, J = 13.0 Hz, 1 H, CH_2), 2.55 (s, 3 H, NCH_3), 2.77–3.48 (m, 5 H, CH_2), 3.84 (m, 2 H, CH_2), 7.16–7.39 (m, 6 H, Ar), 7.79 (m, 1 H, Ar), 8.38 (d, J = 5.2 Hz, 1 H, Ar) ppm.

3d: Like **3b** from HSC_6H_5 (0.115 g, 1.00 mmol), 1.00 mmol of $NaOCH_3$, and **L^3·**ZnBr (0.369 g, 1.00 mmol). Yield 0.224 g (56%) of **3d** as colorless crystals, m.p. 122 °C. $C_{18}H_{24}N_2S_2Zn$ (397.92): calcd. C 54.33, H 6.08, N 7.04, S 16.12; found C 54.30, H 6.29, N 6.99, S 15.43. IR (KBr): $\tilde{\nu}$ = 1608 s, 1578 s cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.18 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.49 (d, J = 13.0 Hz, 1 H, CH_2), 2.66 (s, 3 H, NCH_3), 2.74–3.20 (m, 5 H, CH_2), 6.90–6.95 (m, 3 H, Ar), 7.31–7.44 (m, 4 H, Ar), 7.92 (m, 1 H, Ar), 8.58 (d, J = 5.2 Hz, 1 H, Ar) ppm.

3e: Like **3c** from $HSC_6H_4NO_2$ (0.103 g, 0.66 mmol), 0.66 mmol of $NaOCH_3$, and **L^3·**ZnBr (0.244 g, 0.66 mmol). Yield 0.202 g (69%) of **3e** as yellow crystals, m.p. 81 °C. $C_{18}H_{23}N_3S_2O_2Zn$ (442.92): calcd. C 48.81, H 5.23, N 9.49, S 14.48; found C 48.50, H 5.05, N 9.30, S 14.28. IR (KBr): $\tilde{\nu}$ = 1609 s, 1569 s cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 2.54 (d, J = 13.0 Hz, 1 H, CH_2), 2.73 (s, 3 H, NCH_3), 2.80–3.47 (m, 5 H, CH_2), 7.33 (d, J = 7.8 Hz, 1 H, Ar), 7.44 (t, J = 6.5 Hz, 1 H, Ar), 7.73 (d, J = 8.8 Hz, 2 H, Ar), 7.84–7.93 (m, 3 H, Ar), 8.72 (d, J = 1.0 Hz, 1 H, Ar) ppm.

3f: Like **3c** from HSC_6F_5 (0.100 g, 0.50 mmol), 0.50 mmol of $NaOCH_3$, and **L^3·**ZnBr (0.184 g, 0.50 mmol). Yield 0.145 g (59%) of **3f** as colorless crystals, m.p. 110 °C. $C_{18}H_{19}F_5N_2S_2Zn$ (487.88): calcd. C 44.31, H 3.93, N 5.74, S 13.15; found C 44.12, H 3.46, N 5.37, S 11.88. IR (KBr): $\tilde{\nu}$ = 1611 s, 1571 m cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3), 2.53 (d, J = 13.0 Hz, 1 H, CH_2), 2.81 (s, 3 H, NCH_3), 2.85–3.53 (m, 5 H, CH_2), 7.31 (d, J = 7.8 Hz, 1 H, Ar), 7.46 (t, J = 6.3 Hz, 1 H, Ar), 7.80 (t, J = 7.2 Hz, 1 H, Ar), 8.85 (d, J = 5.0 Hz, 1 H, Ar) ppm. ^{19}F NMR ($CDCl_3$): δ = –163.3 (s, 2 F), –161.9 (s, 1 F), –133.9 (s, 2 F) ppm.

4d: A solution of **3d** (0.100 g, 0.25 mmol) in 15 mL of chloroform was treated with methyl iodide (0.036 g, 0.25 mmol). After stirring for 3 d the solvent was removed in vacuo, the residue washed with diethyl ether, and dried in vacuo to give 0.078 g (57%) of **4d** as a colorless powder, m.p. 128 °C. $C_{19}H_{27}IN_2S_2Zn$ (539.86): calcd. C 42.27, H 5.04, N 5.19, S 11.14; found C 39.26, H 5.19, N 5.56, S 12.04. IR (KBr): $\tilde{\nu}$ = 1609 s, 1569 m cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.03 (s, 3 H, SCH_3), 2.50 (d, J = 9.2 Hz, 1 H, CH_2), 2.81 (s, 3 H, NCH_3), 2.84–3.48 (m, 5 H, CH_2), 6.96–7.00 (m, 3 H, Ar), 7.10–7.44 (m, 4 H, Ar), 7.83 (br. d, J = 6.2 Hz, 1 H, Ar), 8.87 (br. s, 1 H, Ar) ppm.

4e: Like **4d** from **3e** (0.090 g, 0.20 mmol) and methyl iodide (0.029 g, 0.20 mmol). Yield 0.064 g (54%) of **4e** as a yellow powder, m.p. 53 °C. $C_{19}H_{26}IN_3O_2S_2Zn$ (584.86): calcd. C 39.02, H 4.48, N 7.18, S 10.97; found C 39.30, H 4.64, N 7.02, S 10.67. IR (KBr): $\tilde{\nu}$ = 1611 s, 1570 m cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 2.06 (s, 3 H, SCH_3), 2.54 (s, 1 H, CH_2), 2.65 (s, 3 H, NCH_3), 2.79–3.18 (m, 5 H, CH_2), 7.28 (d, J = 7.2 Hz, 1 H, Ar), 7.61 (d, J = 8.8 Hz, 2 H, Ar), 7.68–7.84 (m, 2 H, Ar), 8.18 (d, J = 9.0 Hz, 2 H, Ar), 8.66 (br. s, 1 H, Ar) ppm.

4f: Like **4d** from **3f** (0.101 g, 0.21 mmol) and methyl iodide (0.030 g, 0.21 mmol). Yield 0.077 g (58%) of **4f** as a colorless powder, m.p. 58 °C. $C_{19}H_{22}F_5IN_2S_2Zn$ (629.81): calcd. C 36.23, H 3.52, N 4.45, S 10.18; found C 34.78, H 3.27, N 5.13, S 9.72. IR (KBr): $\tilde{\nu}$ = 1610 s, 1571 m cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.36 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.11 (s, 3 H, SCH_3), 2.48 (s, 1 H, CH_2), 2.83 (s, 3 H, NCH_3), 2.95–3.66 (m, 5 H, CH_2), 7.27–7.47 (m, 2 H, Ar), 7.68–7.80 (m, 1 H, Ar), 8.67 (br. s, 1 H, Ar) ppm. ^{19}F NMR ($CDCl_3$): δ = –163.1 (s, 2 F), –161.9 (s, 1 F), –132.9 (s, 2 F) ppm.

5d: A solution of **3d** (0.116 g, 0.29 mmol) and $PO(OMe)_3$ (0.041 g, 0.29 mmol) in 15 mL of DMSO was stirred at 80 °C for two weeks. The solvent was then removed by distillation in vacuo. The residue was washed with diethyl ether and dried in vacuo to give 0.116 g (74%) of **5d** as a slightly yellow wax which could not be purified further and hence was identified only by ^{1}H NMR spectroscopy in $CDCl_3$: δ = 1.40 (br. s, 6 H, CH_3), 1.73 (s, 3 H, SCH_3), 2.55–3.39 (m, 9 H, NCH_3/CH_2), 3.63 (d, J = 11.0 Hz, 6 H, OCH_3), 6.90–7.10 (m, 3 H, Ar), 7.32–7.52 (m, 4 H, Ar), 7.86 (t, J = 7.6 Hz, 1 H, Ar), 8.83 (br. s, 1 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 0.91 ppm.

Complex 6. a) From 3d: A solution of **3d** (0.120 g, 0.30 mmol) and methyl iodide (0.214 g, 1.50 mmol) in 15 mL of chloroform was stirred for 3 d. The solvent was then removed in vacuo and the residue extracted with two 10-mL portions of diethyl ether. The remaining product was dried in vacuo to give 0.148 g (88%) of **6** as a colorless powder, m.p. 59 °C. $C_{13}H_{22}I_2N_2SZn$ (557.59): calcd. C 28.00, H 3.98, N 5.02, S 5.75; found C 27.48, H 3.97, N 5.53, S 5.27. IR (KBr): $\tilde{\nu}$ = 1610 s, 1570 m cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ = 1.53 (s, 6 H, CH_3), 2.18 (s, 3 H, SCH_3), 2.91 (s, 3 H, NCH_3), 3.18 (br. s, 2 H, CH_2), 3.41–3.52 (m, 4 H, CH_2), 7.41–7.50 (m, 2 H, Ar), 7.90 (m, 1 H, Ar), 8.87 (br. s, 1 H, Ar) ppm.

The diethyl ether phase was evaporated to dryness and the remaining $CH_3SC_6H_5$ identified by ^{1}H NMR ($CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 7.12–7.28 (m, 5 H, Ph) ppm.

b) From 3e: As before from **3e** (0.100 g, 0.23 mmol) and methyl iodide (0.326 g, 2.30 mmol). Yield 0.113 g (88%) of **6**. Identifica-

Table 1. Crystallographic details.

	1·2 $CHCl_3$	**2a**	**L^3**·ZnCl	**3d**	**3e**	**3f**
Empirical formula	$C_{34}H_{42}Cl_6N_4S_4Zn_2$	$C_{34}H_{44}N_4S_4Zn_2$	$C_{12}H_{19}ClN_2SZn$	$C_{18}H_{24}N_2S_2Zn$	$C_{18}H_{23}N_3O_2S_2Zn$	$C_{18}H_{19}F_5N_2S_2Zn$
Molecular mass	978.49	767.79	324.17	397.88	442.88	487.84
Crystal size (mm)	0.05×0.10×0.10	0.06×0.08×0.4	0.13×0.14×0.35	0.06×0.08×0.15	0.05×0.14×0.20	0.07×0.10×0.22
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
Z	1	1	4	4	4	4
a [Å]	8.801(3)	7.929(2)	8.203(1)	7.645(2)	16.582(3)	10.88(2)
b [Å]	11.201(4)	10.279(2)	14.979(2)	10.716(2)	14.918(3)	17.73(3)
c [Å]	11.656(4)	12.440(2)	11.788(2)	23.273(5)	8.254(2)	11.01(2)
α [°]	102.573(6)	94.38(3)	90	90	90	90
β [°]	91.473(6)	105.75(3)	93.436(2)	90	96.545(4)	98.97(4)
γ [°]	109.623(5)	108.60(3)	90	90	90	90
V [Å³]	1050.3(6)	910(3)	1445.8(4)	1906.6(6)	2028.4(6)	2096(7)
d(calcd.)[g cm^{-3}]	1.55	1.40	1.49	1.39	1.45	1.55
μ(Mo-K_α) [mm^{-1}]	1.75	1.58	2.01	1.51	1.43	1.42
hkl range	h: –11 to 11	h: –10 to 10	h: –10 to 10	h: –7 to 10	h: –20 to 23	h: –14 to 14
	k: –14 to 14	k: –14 to 13	k: –19 to 19	k: –8 to 13	k: –15 to 19	k: –23 to 22
	l: –15 to 15	l: –16 to 15	l: –15 to 15	l: –30 to 9	l: –10 to 10	l: –14 to 14
Measured reflections	9099	8042	12 971	7110	13 303	18 628
Independent reflections	4801	4203	3552	4233	5414	5061
Observed reflections [$I > 2\sigma(I)$]	3070	2211	2944	1918	2492	1628
parameters	221	199	154	208	235	253
Refined reflections	4801	4203	3552	4233	5414	5061
R_1 (obsd.refl.)	0.063	0.038	0.028	0.062	0.049	0.041
wR_2 (all refl.)	0.178	0.078	0.082	0.222	0.130	0.147
Res. electron density [e Å^{-3}]	+1.2/–1.6	+0.9/–1.0	+0.7/–0.6	+0.5/–0.7	+0.5/–0.7	+0.4/–0.6

tion of $CH_3SC_6H_4$-*p*-NO_2 by ^{1}H NMR ($CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 7.19–7.25 (m, 2 H, Ar), 8.03–8.10 (m, 2 H, Ar) ppm.

c) From 3f: As before from **3f** (0.050 g, 0.10 mmol) and methyl iodide (0.142 g, 1.00 mmol). Yield 0.047 g (84%) of **6**. Identification of $CH_3SC_6F_5$ by ^{1}H NMR ($CDCl_3$): δ = 2.47 (CH_3) ppm.

Complex 7: Complex **3d** (0.122 g, 0.31 mmol) and trimethyl phosphate (0.317 g, 1.55 mmol) in 15 mL of DMSO were stirred at 80 °C for two weeks. The solvent was then removed by distillation in vacuo. The residue was extracted with two 10-mL portions of diethyl ether and dried in vacuo to give 0.121 g (71%) of **7** as an impure, waxy material which was identified by ^{1}H NMR ($CDCl_3$): δ = 1.45 (s, 6 H, CH_3), 2.06 (d, J = 2.6 Hz, 3 H, SCH_3), 2.61 (s, 3 H, NCH_3), 2.72–3.05 (m, 4 H, CH_2), 3.32 (s, 2 H, CH_2), 3.64 (d, J = 11.0 Hz, 12 H, OCH_3), 7.15–7.23 (m, 2 H, Ar), 7.46 (t, J = 8.0 Hz, 1 H, Ar), 7.72 (d, J = 6.0 Hz, 1 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 0.55 ppm.

The diethyl ether phase was evaporated to dryness and the remaining $CH_3SC_6H_5$ identified by ^{1}H NMR spectroscopy as above.

Structure Determinations:[28] Crystals were obtained as described above. Diffraction data were recorded at room temp. for **3d** and **3f** and at 220 K for **1**, **2a**, **3e**, and **L^3**·ZnCl with a Bruker Smart CCD diffractometer. Empirical absorption corrections (SADABS) were applied for **1**, **2a**, and **L^3**·ZnCl. The structures were solved and refined anisotropically with the SHELX program suite.[29] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5-times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL.[30] Table 1 lists the crystallographic data.

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[1] G. Parkin, *Chem. Rev.* **2004**, *104*, 699–767.
[2] R. G. Matthews, *Acc. Chem. Res.* **2001**, *34*, 681–689.
[3] U. Brand, M. Rombach, H. Vahrenkamp, *Chem. Commun.* **1998**, 2717–2718.
[4] U. Brand, M. Rombach, J. Seebacher, H. Vahrenkamp, *Inorg. Chem.* **2001**, *40*, 6151–6157.
[5] J. Seebacher, M. Ji, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **2004**, 409–417.
[6] C. A. Grapperhaus, T. Tuntulani, J. H. Reibenspies, M. Y. Darensbourg, *Inorg. Chem.* **1998**, *37*, 4052–4058.
[7] B. M. Bridgewater, T. Fillebeen, R. A. Friesner, G. Parkin, *J. Chem. Soc., Dalton Trans.* **2000**, 4494–4496.
[8] B. S. Hammes, C. J. Carrano, *Inorg. Chem.* **2001**, *40*, 919–927.
[9] C. R. Warthen, B. S. Hammes, D. C. Crans, C. J. Carrano, *J. Biol. Inorg. Chem.* **2001**, *6*, 82–90.
[10] M. Machuqueiro, T. Darbre, *J. Inorg. Biochem.* **2003**, *94*, 193–196.
[11] S. J. Chiou, J. Innocent, C. G. Riordan, K. C. Lam. L. Liable-Sands, A. L. Rheingold, *Inorg. Chem.* **2000**, *39*, 4347–4353.
[12] U. Brand, H. Vahrenkamp, *Inorg. Chem.* **1995**, *34*, 3285–3293.
[13] U. Brand, H. Vahrenkamp, *Chem. Ber.* **1996**, *129*, 435–440.
[14] U. Brand, H. Vahrenkamp, *Inorg. Chim. Acta* **2000**, *308*, 97–102.
[15] A. Trösch, H. Vahrenkamp, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2523–2527.
[16] M. Shu, R. Walz, B. Wu, J. Seebacher, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **2003**, 2502–2511.
[17] B. Benkmil, M. Ji, H. Vahrenkamp, *Inorg. Chem.* **2004**, *43*, 8212–8214.
[18] R. R. Holmes, *Acc. Chem. Res.* **1979**, *12*, 257–266.
[19] B. Kaptein, L. Wang-Griffin, G. Barf, R. M. Kellogg, *J. Chem. Soc., Chem. Commun.* **1987**, 1457–1459.
[20] S. C. Chang, R. D. Sommer, A. L. Rheingold, D. P. Goldberg, *Chem. Commun.* **2001**, 2396–2397.
[21] S. C. Chang, V. V. Karambelkar, R. C. Di Targiani, D. P. Goldberg, *Inorg. Chem.* **2001**, *40*, 194–195.

[22] S. C. Chang, V. V. Karambelkar, R. D. Sommer, A. L. Rheingold, D. P. Goldberg, *Inorg. Chem.* **2002**, *41*, 239–248.
[23] B. S. Hammes, C. J. Carrano, *Inorg. Chem.* **1999**, *38*, 4593–4600.
[24] B. S. Hammes, C. J. Carrano, *J. Chem. Soc., Dalton Trans.* **2000**, 3304–3309.
[25] L. C. Myers, M. P. Terranova, A. E. Ferentz, G. Wanger, G. L. Verdine, *Science* **1993**, *261*, 1164–1167.
[26] J. J. Wilker, S. Lippard, *Inorg. Chem.* **1997**, *36*, 969–978.
[27] M. Förster, R. Burth, A. K. Powell, T. Eiche, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 2643–2648.
[28] CCDC-254409 (for **1**), -254410 (for **2a**), -254411 (for **L3·ZnCl**), -254412 (for **3d**), -25440 254413 (for **3e**), and -254414 (for **3f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[29] *SHELXTL* program package for the Bruker Smart CCD diffractometer, version 5.1, **2002**.
[30] E. Keller, *SCHAKAL* for Windows, University of Freiburg, **1999**.

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