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Synthesis and Coordination Properties of Chelating Dithiophenolate Ligands

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Chelating 3,3′-R^1-5,5′-R^2-2,2′-dithiobiphenyl ligands ($R^1 = R^2 =$ Cl, **4a**; $R^1 = R^2 =$ ^{t}Bu, **4b**; $R^1 =$ allyl, $R^2 =$ H, **4c**) and the 2,2′-methylenedibenzenethiol ligand (**4d**) were synthesized from the corresponding diols (**1a**−**1d**) via a three-step procedure involving a Miyazaki−Newman−Kwart rearrangement. Zinc complexes and a tin complex (for **4c**) have been prepared to explore their coordination potential, and the substitution pattern, as well as the chelate ring size, is shown to severely effect their ligating properties. Four of the complexes have been characterized crystallographically in the solid state, and the nuclearity of the zinc complexes in solution has been studied by diffusion-ordered NMR spectroscopy. Depending on the ligand, zinc complexes $[(\mathbf{4})Zn(4,4'\text{-}^t\text{Bu-bipyridine})]_n$ (**5a**−**d**) are monomeric ($n = 1$; **4b**, **4c**), monomeric in solution and dimeric in the solid state ($n = 1, 2$; **4a**), or dimeric overall ($n = 2$; **4d**). The tin complex (**4c**)$SnPh_2$ (**6c**) was additionally synthesized to prove the coordinating abilities of the allyl substituted ligand **4c**.

Introduction

Although thiophenolate-based ligand systems coordinated to transition metals have been successfully applied in homogeneous catalysis[1] and bioinorganic model chemistry,[2] they are still relatively unexplored compared to the corresponding phenolates. Particular classes of chelating dithiolate ligands that have been studied extensively are the 1,1-dithiolates (such as dithiocarbamate, xanthate, etc.)[3−5] and 1,2-dithiolates (mainly dithiolene type ligands[3] and related systems such as 1,2-benzenedithiol,[6] 2,3-dimercaptomaleonitrile,[7] 4,5-dimercapto-1,3-dithiole-2-thione,[8] etc.). In contrast, reports on "non-geminal" and "non-vicinal" chelating dithiols with larger chelate ring sizes are comparatively rare. This is particularly true for thio-analogues of the widely used 2,2′-biphenols and binaphthols,[9] since only very few thio-derivatives of the latter systems are known in addition to the parent 2,2′-dithiobiphenyl.[10,11] Formally, 1,1′-biphenyl-2,2′-dithiolate-coordinated metal complexes can be regarded as vinylene-extended analogues of metal dithiolenes. For steric and geometric reasons, however, the 7-membered MS_2C_4-chelate rings in the biphenyl-based complexes need to diverge from planarity, in contrast to the often planar 5-membered MS_2C_2-chelates in dithiolene-based systems.[12] Thus, 2,2′-dithiobiphenyl-type ligand systems represent a useful supplement to dithiolenes if S-chelated complexes with decreased π-stacking tendency[12] or diminished redox-activities are required (compared to dithiolenes,[13] ligand-centered oxidations in biphenyls seem to be unlikely as the resonance stabilization of the aromatic systems would be perturbed).

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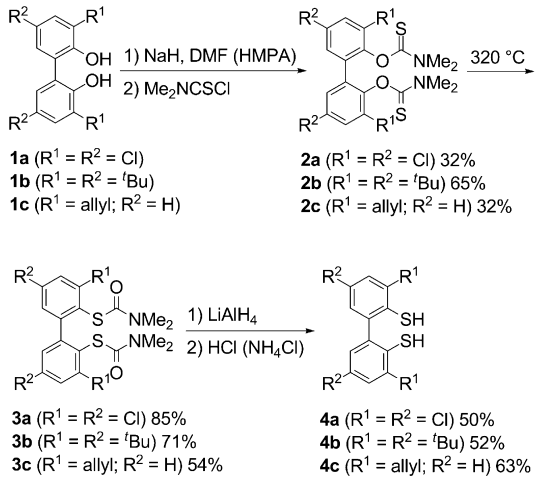
Scheme 1. Synthesis of Substituted 2,2′-Dithiobiphenyl Ligands

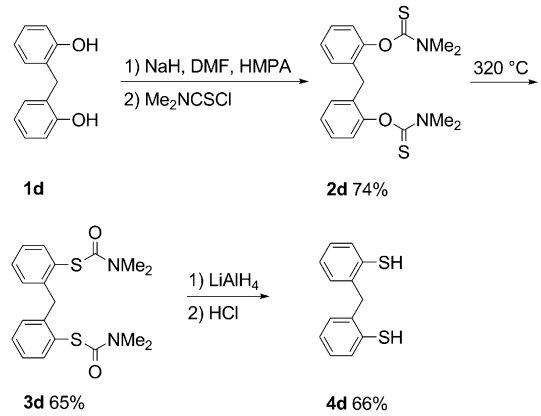


In view of the versatile properties and wide-ranging applications of metal dithiolenes,[14] exploration of biphenyl-based bidentate thiophenols with variable substitution patterns (to modulate electronic as well as steric effects) seemed to be promising and of general interest. In this context we here report the preparation of three new biphenyl-based sulfur ligands, as well as the methylene-extended 2,2′-methylenedibenzenethiol system. The latter non-conjugated analogue was prepared to study the effect of the chelate ring size. A first glance at the coordination chemistry of this set of ligands has been obtained for the corresponding zinc or tin complexes.

Results and Discussion

To access the sought-after substituted 2,2′-dithiobiphenyl ligands via a Miyazaki−Newman−Kwart rearrangement strategy[15] (it was recently suggested to use this term instead of Newman−Kwart rearrangement, taking important studies of Miyazaki et al. on the mechanism of thione-to-thiol rearrangements into account[16]), the biphenols **1a**−**1c** serve as convenient starting material available according to literature methods.[17,18] The corresponding dithiols could now be obtained in a three step synthetic sequence (Scheme 1). After deprotonation with sodium hydride, the biphenolates were treated with dimethylcarbamothioic chloride. Although an excess of both base and dimethylcarbamothioic chloride was used, the reactions afforded the desired bis-*O*-thiocarbamate esters **2a** and **2c** only in moderate yields of around 30%, as an equal amount of mono-*O*-thiocarbamate ester remained. In some cases, this procedure could be improved by adding a small amount of HMPA. After purification, the neat compounds **2a**−**2c** were heated to 320 °C for up to 4 h. At this temperature, a Miyazaki−Newman−Kwart rearrangement takes place to give the bis-*S*-thiocarbamate esters **3a**−**3c** in yields of 54 to 85%. Formation of the free dithiols **4a**−**4c** was achieved by reduction with $LiAlH_4$ and subsequent acidic workup. To prevent possible oxidation to internal disulfides, the workup was carried out under inert nitrogen atmosphere. While HCl was used in the workup of the other dithiols, 3,3′-diallyl-2,2′-dithiobiphenyl (**4c**) could not be obtained using the above standard procedure. Instead, the formation of fused five-membered rings via intramolecular hydrosulfuration was observed. To avoid this known type of reaction,[19] aqueous NH_4Cl was used instead. Under these milder conditions, clean conversion to the free dithiol took place.

Scheme 2. Synthesis of 2,2′-Methylenedibenzenethiol



The synthesis of the methylene-bridged derivative 2,2′-methylenedibenzenethiol **4d** was performed in a similar manner, starting from diol **1d** (Scheme 2). Preparation of the required **1d** was carried out with slight modifications of literature methods via condensation of 2,4-di-*tert*-butylphenol with *para*-formaldehyde and subsequent stepwise removal of all *tert*-butyl protective groups (experimental details are provided in the Supporting Information).[20−22] Formation of the bis-*O*-thiocarbamate ester **2d** and separation from the undesired mono-*O*-thiocarbamate ester was straightforward in this case (74% yield). Rearrangement and reductive carbamate cleavage using the standard protocol afforded the free dithiol **4d**.

In the ^1H and ^{13}C NMR spectra of the *O*-carbamate ester compounds **2b** and **2d**, two signals are found for the methyl groups attached to the carbamate nitrogen atoms. This indicates a slow rotation around the C−N bond because of delocalization of the carbamate double bond. The corresponding spectra of compounds **2a** and **2c** show even four methyl signals, indicating that a barrier also exists for the rotation of the entire ester group around the aryl-O bond. At low temperature (−60 °C), three distinct sets of signals (i.e., 6 methyl signals) are observed for **2a** and **2c**.

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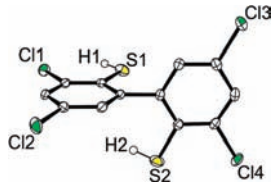


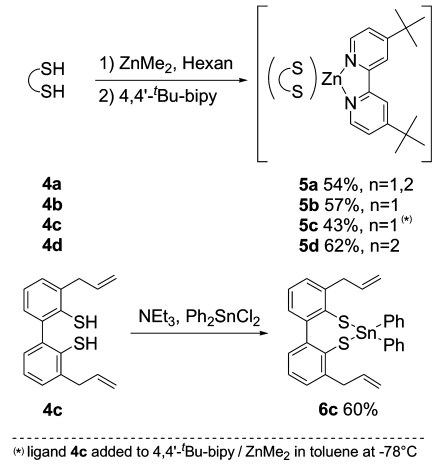
Figure 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP, 50% probability thermal ellipsoids) plots of the molecular structure of **4a**. Selected atom distances (Å) and angles (deg): S1−H1 1.02(4), S2−H2 1.02(4), S1−C2 1.7581(16), S2−C2′ 1.7565(16), C1−C1′ 1.498(2), H1−S1−C2 94.6(19), H2−S2−C2′ 106(2), C2−C1−C1′-C2′ 90.61(19).

The observations in the NMR spectra are in agreement with crystal structures of related compounds,[15] where both the aryl-aryl and aryl *O*-carbamate ester groups are twisted nearly 90° with respect to each other, resulting in two sterically favored (racemic) diastereomers: a C_2-symmetric species with the same relative orientation of the ester groups, producing one set of NMR peaks and a completely asymmetric species with opposite orientation of the ester groups, producing a split set of peaks with a 1:1 integral ratio. At −60 °C, the signals of the split set slowly interconvert through rotation of the aryl-aryl bond, while at room temperature most of them have coalesced, as expected for an energetic barrier of about 60 kJ/mol.[23] The barriers for rotation of the ester group and the carbamate C−N bond are much higher (both about 75 kJ/mol), so that separate, albeit broad, signals are still observable at room temperature.

At closer inspection, three sets of peaks are also observed in the NMR spectra of **2b** but with a very minor population (about 6%) of the asymmetric isomer. None of the peaks shows dynamic exchange up to 50 °C, presumably because of the steric bulk of the *tert*-butyl groups which locks the molecules in their individual conformations. In contrast, compound **2d** with the flexible methylene bridge seems to undergo rapid transitions between all conformations as the spectra show single peaks without dynamic effects.

After the Miyazaki−Newman−Kwart rearrangement, only a single signal is found for the N-bonded methyl groups, which is in agreement with earlier reports for *S*-thiocarbamate esters.[24] Also, the ^{13}C resonance of the thione carbon undergoes a large upfield shift from about 186 to about 166 ppm. Thus, formation of the bis-*S*-thiocarbamate esters **3a**−**3d** can be monitored by NMR and IR (thione bands at 1530 cm^{-1} to 1550 cm^{-1} versus carbonyl bands at ∼1670 cm^{-1}) spectroscopy. As expected, bond rotations in the free dithiols **4a**−**4d** are not hindered, which is evident from sharp ^{1}H NMR signals for all aromatic resonances. Compound **4a** could be crystallized from THF/pentane to give single crystals suitable for X-ray diffraction. This is a rare example of a structurally characterized 2,2′-dithiobiphenyl derivative (Figure 1; at present 4,4′-diamino-2,2′,6,6′-tetrathio-1,1′-biphenyl is the only other crystallographically characterized biphenyl derivative with two free thiol groups in 2,2′-position[25]). The 1,1′-linked phenyl rings are found perpendicular to each other with a dihedral angle C2−C1−C1′−C2′ of 90.61(19)°.

Scheme 3. Synthesis of Zinc Complexes **5** and Tin Complex **6c**



To probe the general coordination chemistry of the free ligands **4a**−**4d**, zinc was thought as a suitable d-block metal for several reasons: Inter alia, diamagnetic zinc allows useful investigations by NMR spectroscopy, and *S*-coordination is prominent in various biological zinc sites. In view of the relevance of S_2N_2-ligated zinc species as biomimetic model compounds for the most common zinc finger motif,[26] 4,4′-di-*tert*-butylbipyridine was utilized as coligand in the present work. Synthesis of the complexes **5a**, **5b**, and **5d** was carried out in a two step procedure according to Scheme 3. Reaction of dimethylzinc with the free ligands results in the formation of polymeric thiophenolate-zinc species, probably because of the bridging tendency of thiophenolates. These sparingly soluble intermediates were filtered off and subsequently reacted with 4,4′-di-*tert*-butylbipyridine in benzene at reflux temperature, causing the polymers to break up (a similar synthetic methodology was previously applied in the synthesis of some related ZnO_2N_2 and CdO_2N_2 complexes[27]). **5a**, **5b**, and **5d** were isolated in 54 to 62% yield, but **5c** could not be obtained this way. Examination of the polymeric mixture obtained after reaction of **4c** with $ZnMe_2$ by ^{1}H NMR spectroscopy in DMSO-d$_6$ revealed an unwanted reactivity of dimethylzinc with the allyl residues, indicated by the absence of all olefinic proton resonances, even in high dilution and low temperature. However, an attack of the highly reactive dimethylzinc on the allyl group could be avoided by changing the reaction sequence. Addition of dimethylzinc to a toluene solution of 4,4′-di-*tert*-butylbipyridine at −78 °C yielded the less reactive (4,4′-di-*tert*-butylbipyridine)$ZnMe_2$ complex which then reacted smoothly with **4c** to give **5c**.

It was previously stated that combining chelating aromatic thiols with nitrogen donor coligands on a zinc center in a ZnS_2N_2 stoichiometry generally results in the formation of mononuclear complexes.[28] In contrast to this, however, we observed a ligand dependent nuclearity for the ZnS_2N_2

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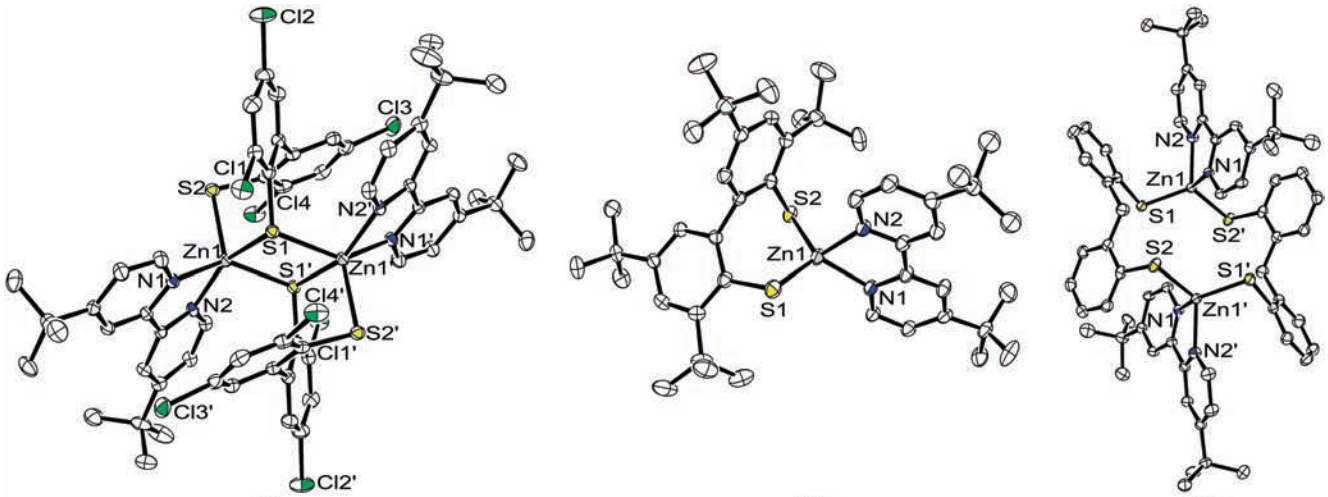

5a **5b** **5d**

Figure 2. ORTEP plots (50% probability thermal ellipsoids) of the molecular structures of **5a**, **5b**, and **5d**. Selected atom distances (Å) and angles (deg) for **5a** (crystallized by slow evaporation of a complex solution in CH_2Cl_2): Zn1−S1 2.5721(7), Zn1−S2 2.3071(6), Zn1−N1 2.104(2), Zn1−N2 2.153(2), Zn1−S1′ 2.3959(6), Zn1···Zn1′ 3.7493(6), N1−Zn1−N2 76.44(8), N1−Zn1−S2 108.66(6), N2−Zn1−S2 112.66(6), N1−Zn1−S1′ 139.57(6), N2−Zn1−S1′ 91.48(5), S2−Zn1−S1′ 111.59(2), N1−Zn1−S1 92.64(6), N2−Zn1−S1 154.64(6), S2−Zn1−S1 92.43(2), S1′−Zn1-S1 82.07(2), Zn1′−S1-Zn1 97.93(2). Selected atom distances (Å) and angles (deg) for **5b** (crystallized by diffusion of hexane into a complex solution in THF): Zn1−S1 2.2592(9), Zn1−S2 2.2653(9), Zn1−N1 2.101(3), Zn1−N2 2.091(3), N2−Zn1−N1 78.84(10), N2−Zn1−S1 102.75(8), N1−Zn1−S1 120.87(8), N2−Zn1−S2 114.61(8), N1−Zn1−S2 114.66(8), S1−Zn1−S2 117.31(3). Selected atom distances (Å) and angles (deg) for **5d** (crystallized by slow evaporation of a complex solution in CH_2Cl_2): Zn1−S1 2.2463(5), Zn1−S2′ 2.2681(4), Zn1−N1 2.0647(13), Zn1−N2 2.0894(14), Zn1···Zn1′ 5.6843(4), N1−Zn1−N2 78.78(5), N1−Zn1−S1 121.54(4), N2−Zn1−S1 110.06(4), N1−Zn1−S2′ 106.29(4), N2−Zn1−S2′ 121.03(4), S1−Zn1−S2′ 114.877(18).

complexes **5a**−**5d**. In the solid state **5b** is found to be monomeric, most likely because of the sterically demanding *tert*-butyl substituents, whereas **5a** and **5d** are found to be dimeric (Figure 2). The coordination environment in **5b** is strongly distorted from tetrahedral ($\tau_4 = 0.86$[29]) because of the acute angle N1−Zn1−N2 (78.84(10)°) imposed by the rigid bipyridine. The aryl rings of the dithiolate are nearly perpendicular with respect to each other (twisted by 88.48(9)°). The zinc atoms in dimerized **5a** ligated by the sterically less hindered ligand **4a** are five-coordinated, as one of the thiolate-S from each ligand adopts a bridging position. The Zn···Zn separation in the resulting Zn_2S_2 diamond core is 3.75 Å. The coordination polyhedra of both crystallographically equivalent zinc atoms are best described as distorted square pyramids ($\tau_5 = 0.25$[30]) with the basal planes through the nitrogen and the bridging sulfur atoms. Compared to the free ligand **4a**, a reduced twist angle between both aryl ring planes of the dithiobiphenolate is observed (60.19(8)°) for **5a**. Interestingly, the zinc atoms in **5d** are tetrahedral (distorted, $\tau_4 = 0.83$[29]) with both ligands bridging the two zinc atoms to form a 16-membered metalla-macrocycle (Figure 2, right). Most likely, the large chelate ring size disfavors a chelate situation, while the higher flexibility of the methylene-extended system **4d** (compared to **4a**−**4c**) permits the formation of this unusual macrocyclic motif. It should be noted, however, that bidentate ligation of **4d** to a single metal is possible too, as this ligand can be successfully applied in the coordination to a [2Fe-2S] cluster core affording tetrahedral iron incorporated in an eight-membered chelate ring.[31] The high flexibility of the complete metalla-macrocycle is apparent from comparison of the molecular structures found for **5d** and **5d′** (the latter containing two molecules of noncoordinated CH_2Cl_2 per Zn_2 unit, see Supporting Information, Figure S44). All Zn−S and Zn−N bond distances (less pronounced effect for Zn−N distances) and related angles at the zinc atoms differ to some extent, although an almost identical $\tau_4 = 0.84$[29] is observed, causing a significant difference in the measured Zn···Zn separation (Zn1···Zn1′ ∼5.7 Å in **5d** versus Zn1···Zn1′ ∼6.0 Å in **5d′**). It should be mentioned that compounds **5a** and **5b** represent the first structurally characterized 2,2′-dithiobiphenolate-coordinated ZnS_2N_2 complexes and **5d/5d′** the only crystallographically characterized zinc complex ligated by 2,2′-methylenedibezenethiolate (derivatives). Comparison with structures for the related mononuclear $(PhS)_2Zn(bipy)$ analogues[32] with non-chelating thiophenolates reveals that the Zn−S distances for **5b** and **5d/5d′** are in the usual range (Zn−S ∼2.3 Å), whereas Zn−S bond lengths involving the bridging sulfur atoms in **5a** are somewhat elongated (Zn1−S1 2.5721(7) Å, Zn1−S1′ 2.3959(6) Å). The Zn−N distances (∼2.1 ± 0.05 Å) and angles N−Zn−N (∼77 ± 2°) are very similar for all type-**5** complexes and in accordance with those observed for the $(PhS)_2Zn(bipy)$ analogues. As expected,

(29) The τ_4 value has been proposed as a simple geometry index to quantify the distortion from tetrahedral geometry ($\tau_4 = 1$) for four-coordinate species and is calculated by $\tau_4 = 1/141° \times (360° - \alpha - \beta)$, with α and β defined as the two largest angles (Ligand)−(Metal)−(Ligand) in the four-coordinate complex: Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.

(30) The τ_5 value has been proposed as a simple geometry index to quantify the distortion from trigonal bipyramidal geometry ($\tau_5 = 1$) for five-coordinate species and is calculated by $\tau_5 = 1/60° \times (\beta - \alpha)$, with α and β defined as the two largest angles (Ligand)−(Metal)−(Ligand) in the five-coordinate complex. Thus, τ_5 values for ideally square pyramidal five-coordinate complexes are equal to zero: (a) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

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however, angles S−Zn−S in the $(PhS)_2Zn(bipy)$ complexes are significantly different (∼125°) from those reported herein because of the less bendable chelating dithio ligands in the type-**5** compounds. The related dithiolene-coordinated complexes $[Zn(bdt)(bipy)]_2$ (bdt = 1,2−1,2-benzenedithiolate)[33] and $[Zn(dmit)(bipy)]_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate),[34] both characterized crystallographically, exhibit Zn−N distances (2.104(2) Å to 2.1857(14) Å) and N−Zn−N angles (74.91(5)°/76.06(8)°) in a similar range (compared to $(PhS)_2Zn(bipy)$ and all type **5** complexes). In this context it should be noted that the latter dimeric $[Zn\{S_2N_2\}]_2$ systems adopt geometries comparable to **5a**, each containing two bridging thiolates in a central Zn_2S_2-rhomb. Both upper dithiolene-coordinated analogues, as well as **5a**, display Zn−S distances to the terminal thiolates (2.31 ± 0.03 Å) that are somewhat shorter than those Zn−S distances to the bridging sulfur atoms (∼2.39 Å to ∼2.58 Å). Mononuclear type-**5b** complexes were also observed in dithiolene-ligated systems with ZnN_2S_2 stoichiometry, for example, if sterically demanding 2,2′-biquinolines were applied instead of 2,2′-bipyridines.[35,36] Prominent structural parameters again agree well with those observed in this study. For the natural zinc-binding boar-TP2 domain (containing three Cys_2His_2 zinc finger motifs, each binding one zinc ion), averaged Zn−S and Zn−N distances were determined by EXAFS analysis to be 2.36 Å and 2.01 Å, respectively.[37]

The zinc complexes **5a**−**5d** were also investigated by variable temperature (VT) NMR in CD_2Cl_2. At room temperature, all four complexes show a single set of ^1H and ^{13}C signals. Strong nuclear Overhauser effect (NOE) crosspeaks between the 2,2′ protons of bipyridine and the 3,3′-^{t}Bu group of **5b**, the allyl group of **5c,** and the CH_2 group of **5d**, respectively, verify that bipyridine and the thiolate ligand are simultaneously coordinated to Zn. Upon cooling, the ^1H signals of **5a**, **5b**, and **5c** broaden somewhat but otherwise remain unaffected down to −75 °C, indicating in all three cases the presence of a single stable species in solution. In contrast, the ^1H signals of **5d** already start to broaden at −25 °C and, at about −50 °C, split into two distinct sets in a 2:1 ratio that become reasonably resolved at −75 °C (Supporting Information, Figure S48) At this temperature, the CH_2 group of the major species still appears as a singlet, while that of the minor species is split into an AB spin system. Again, both species show the characteristic NOE crosspeaks between the CH_2 protons and the respective bipy-2,2′ protons, underlining the strong preference for mixed ZnS_2N_2 coordination.[28]

To gain further insight into the aggregation/nuclearity of the four zinc complexes in solution, we used diffusion-ordered spectroscopy (DOSY NMR) to measure diffusion coefficients of the complexes and the corresponding free ligands **4a**−**4d**. We then compared the molecular radii obtained via the Stokes−Einstein relation to the radii calculated from crystallographic volumes, where the volumes of the dithiols **4b** and **4d** were approximated by that of the previously characterized corresponding diols **1b**[38] and **1d**[39] (details are given in the Supporting Information).[40] The solution ratio $R_{complex}/R_{ligand}$ of 1.4 for **5a** (calcd from X-ray for monomeric species, 1.3; calcd for dimeric species, 1.7) and 1.4 for **5b** (calcd for monomeric species, 1.5; calcd for dimeric species, 1.9), together with the variable temperature data, indicates that both complexes are momomeric in solution and adopt a structure similar to that observed for **5b** in the solid state. Apparently, the dimeric solid state structure determined for **5a** by X-ray diffraction is broken up when dissolved in CD_2Cl_2 to give the corresponding monomeric species [LZn(bipy)]. No crystals suitable for X-ray diffraction could be obtained for complex **5c**, but the solution ratio $R_{complex}/R_{ligand}$ of 1.5 is similar to **5a** and **5b** and thus suggests a monomeric composition in solution.

In the case of **5d**, the results from the DOSY NMR spectra are less clear: Although the ratio $R_{complex}/R_{ligand}$ of 1.8 (calcd from X-ray for monomeric species, 1.4; calcd for dimeric species, 1.8) would suggest a dimeric species in solution, the measured absolute value $R_{complex}$ of 5.0 Å agrees better with that calculated for a monomeric species (5.6 Å) than with that calculated for a dimeric species (7.0 Å). Repeat of the DOSY experiment at −95 °C (at higher temperatures the experiment is still affected by exchange during the diffusion period) yielded different diffusion coefficients for the two species that can be translated into relative molecular radii of 5:4 for the major to minor species (Supporting Information, Figure S48). From this we concluded that in solution **5d** exists as a monomer−dimer equilibrium, possibly with the dimer assuming the macrocyclic structure observed in the solid state, and the momomer assuming a structure similar to that of **5b**. This conclusion is further supported by our observation that the equilibrium is shifted toward the monomeric species upon dilution and increase of temperature (entropy effect). According to this model, the interconversion between the monomeric and dimeric forms of **5d** requires breaking and reforming of two Zn−S bonds, a process for which an energetic barrier of about 10 kcal/mol (or 42 kJ/mol) can be calculated from the coalescence temperature.

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(40) A crystallographically characterized *tert*-butyl substituted derivative of 2,2′- methylenedibenzenethiolate was previously reported (without explicit experimental procedure); estimation of the molecular volume for the unsubstituted analogue, however, is difficult from that crystal data because of the sterically demanding *tert*-butyl groups: Hiller, W.; Rundel, W. *Acta Crystallogr.* **1993**, *C49*, 1127–1128.

Figure 3. ORTEP plot (50% probability thermal ellipsoids) of the molecular structure of **6c** (crystallized by diffusion of pentane into a complex solution in THF). Selected atom distances (Å) and angles (deg): Sn1−C_{Ph} 2.1221(16), Sn1−C_{Ph}' 2.1221(16), Sn1−S1 2.357(8), Sn1−S2 2.448(7), C_{Ph}−Sn1−C_{Ph}' 115.68(8), C_{Ph}−Sn1−S1 120.00(14), C_{Ph}'−Sn1−S1 102.20(19), C_{Ph}−Sn1−S2 105.18(17), C_{Ph}'−Sn1−S2 112.26(14), S1−Sn1−S2 100.71(4).

This process may proceed via an intermediate where two new bonds between Zn and a bridging sulfur atom are already formed, just as observed in the structure of **5a** (Zn1−S1′ and Zn1′−S1). Release of the other two bonds of the central Zn2S2 diamond (Zn1−S1 and Zn1′−S1′) would then result in the macrocyclic dimeric structure. Conformational rearrangements within the dimeric structure, such as a boat−boat ring-flip of the metalla-macrocycle are still fast at −95 °C, possibly because of the high flexibility of the methylene-bridged ligand **4d**. Interestingly, two doublets for the methylene-linkage in the monomeric species of **5d** are detected at low temperatures, indicating a slower ring-flip isomerization of the anticipated eight-membered chelate ring.

The coordination potential of **4c** was further demonstrated here by preparation of the corresponding diphenyl tin complex **6c**, obtained by reaction of the dithiol with diphenyltindichloride in the presence of triethylamine (Scheme 3).[41] As expected, the tin atom has a distorted tetrahedral coordination sphere (Figure 3). Bond lengths (Sn−C 2.1221(16) Å, Sn−S 2.357(8)−2.448(7) Å), as well as angles around the Sn atom (100.71(4)−120.00(14)°), are comparable to the related compound $(PhS)_2SnPh_2$ with non-chelating thiophenolates.[42] The two phenyl groups of the biphenyl moiety in **6c** are twisted by 62.4(4)°. It should be mentioned that ligand precursor **3c**, ligand **4c**, and its complexes (e.g., **5c** and **6c**) bear the potential for further derivatization on the allyl residue by, for example, olefin metathesis, hydrometalation including hydroboration, McMurry coupling, click-chemistry, and various palladium catalyzed C−C coupling reactions.

Conclusions

Efficient syntheses have been developed for chelating 3,3′-R^1-5,5′-R^2-2,2′-dithiobiphenyl ligands as well as for the related 2,2′-methylenedibenzenethiol scaffold, and a set of such ligands has been fully characterized. Their coordination potential has been probed with zinc(II), using bipyridine as a coligand, and tin(IV) in the case of the allyl-substitued derivative, and a versatile (and in some cases dynamic) behavior has been elucidated by VT and DOSY NMR spectroscopy in solution as well as by X-ray crystallography in the solid state. The tendency of the thiophenolate group to bridge two metal ions is reflected in monomer−dimer equilibria, but these strongly depend on the backbone substituents. In view of the widespread use of 2,2′-biphenol and binaphthol ligands in, for example, catalysis, the present thioanalogues promise to find manifold applications.

Experimental Section

All reactions were carried out under an anaerobic and anhydrous atmosphere of dry nitrogen by employing standard Schlenk techniques; all workup procedures were done in air (except the isolation procedure for the moderately air-sensitive compounds **4**, **5**, and **6**). Toluene, pentane, hexanes, and Et_2O were dried over sodium benzophenone ketyl, THF over potassium benzophenone ketyl, DMF over CaH_2, nitromethane, $CDCl_3$ and CCl_4 over P_4O_{10}, and distilled prior to use. NaH was purchased as dispersion in mineral oil, washed repeatedly with hexanes, and dried in vacuum. All other chemicals were used as purchased. Glassware was dried at 120 °C overnight.

NMR Spectroscopy. ^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR, NOESY, and DOSY NMR spectra were recorded on Bruker Avance 500 and 300 MHz spectrometers at 25 °C, unless indicated otherwise. The mixing period used in room temperature NOESY spectra (500 ms) was reduced to 100 ms at −75 °C to prevent spin diffusion. DOSY spectra were recorded with a z-Gradient ramped linearly from 1 to 53 G/cm, bipolar gradient pulses of 2 ms, and a diffusion delay of 70 ms (reduced to 30 ms to prevent exchange). Chemical shifts are reported in ppm relative to residual ^{1}H and ^{13}C signals of $CDCl_3$ at 7.24 ppm and 77.0 ppm, CD_2Cl_2 at 5.32 ppm and 54.0 ppm and C_6D_6 at 7.15 ppm and 128.0 ppm, respectively.

Microanalyses were performed by the "Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen". ESI HRMS was applied where accurate analyses were difficult to obtain. Infrared spectra were recorded on a Digilab Excalibur FTS3000 spectrometer. Melting points were determined using a SRS OptiMelt apparatus. EI mass spectra were measured on a Finnigan MAT 8200, ESI mass spectra on a Thermo Finnigan Trace LCQ spectrometer, ESI HRMS spectra on a Bruker FTICR APEX IV instrument. Compounds 2,2′-dihydroxy-3,3′,5,5′-tetrachlorobiphenyl (**1a**),[17] 2,2′-dihydroxy-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (**1b**),[18] and 2,2′-dihydroxy-3,3′-diallylbiphenyl (**1c**)[17] were synthesized according to published procedures. Compound 2,2′-methylenediphenol (**1d**) was synthesized by modifications of previously reported procedures (details given in the Supporting Information).[20−22]

2,2′-Bis-(*N*,*N*-dimethylthiocarbamoyloxy)-3,3′,5,5′-tetrachlorobiphenyl (2a). To a vigorously stirred solution of 3,3′,5,5′-tetrachlorobiphenyl (**1a**, 20.0 g, 62 mmol) in DMF (160 mL) at 0 °C was added NaH (3.20 g, 133 mmol) in portions during 5 min. After completed addition the reaction mixture was stirred for 3 h at room temperature. Subsequently dimethylcarbamothioic chloride (26.8 g, 218 mmol) was added in portions, and the resulting mixture was stirred for 18 h at 105 °C. After cooling to room temperature, the reaction was quenched by addition of water (650 mL) and acidified with conc. aqueous HCl (37%, 15 mL) to precipitate a brownish sticky solid. The mixture was left standing at 4 °C for 1 h to complete the precipitation. The supernatant was decanted off, and the residual solid dried in vacuum with gentle heating. The obtained brownish solid was stirred in a mixture of hexanes

(41) Compare: Gualtieri, G.; Geib, S. J.; Curran, D. P. *J. Org. Chem.* **2003**, *68*, 5013–5019.
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(240 mL) and chloroform (35 mL) at 70 °C for 6 h and cooled to room temperature again. The gray finely powdered undissolved solid was filtered off and dried in vacuum to afford the crude product (12 g, pure in ^{1}H NMR, but not suitable for Miyazaki−Newman−Kwart rearrangement). Final purification was achieved by column chromatography (silica, hexanes/EtOAc 10:1, TLC's recorded in hexanes/EtOAc 5:2, $R_f \sim 0.5$) to obtain a pure white powder of the product (10.0 g, 20 mmol, 32%). Mp (uncorrected) 212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.15$ (s, 6H, NMe_2), 3.26 (s, 3H, NMe_2), 3.32 (s, 3H, NMe_2), 7.31 (d, 1H, $^4J_{H,H} = 2.4$ Hz, Ar−H), 7.45 (dd, 2H, $^4J_{H,H} = 2.1$ Hz, $^4J_{H,H} = 2.4$ Hz, Ar−H), 7.51 (s_{br}, 1H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 38.4$ (NMe_2), 38.9 (NMe_2), 43.4 (NMe_2), 43.5 (NMe_2), 128.9 (Ar−C), 129.3 (Ar−C), 130.0 (Ar−C), 130.0 (Ar−C), 130.0 (Ar−C), 130.1 (Ar−C), 130.8 (Ar−C), 131.6 (Ar−C), 132.1 (Ar−C), 132.9 (Ar−C), 146.1 (Ar−C), 146.4 (Ar−C), 184.7 (CO), 185.0 (CO). EI-MS: *m/z* (%) = 499 (2) [M^+], 463 (38) [$M^+ - Cl$], 427 (5) [$M^+ - 2$ Cl], 88 (100) [$Me_2NC(S)^+$], 72 (39) [$Me_2NC(O)^+$]. IR (KBr): ν(cm^{-1}) = 1549 (CS, s). Elemental analysis: calcd (%) for $C_{18}H_{16}Cl_4N_2O_2S_2$: C 43.39, H 3.24, N 5.62. Found: C 43.72, H 3.37, N 5.71.

2,2′-Bis-(*N,N*-dimethylcarbamoylthio)-3,3′,5,5′-tetrachlorobiphenyl (3a). A 250 mL Schlenk flask was charged with 2,2′-bis-(*N,N*-dimethylthiocarbamoyloxy)-3,3′,5,5′-tetrachlorobiphenyl (**2a**, 7.0 g, 14 mmol) and heated to 320 °C without agitation for 10 min. The resulting yellow oil solidified at room temperature and was recrystallized from chloroform/hexanes (100 mL/10 mL, reflux to 4 °C) to obtain a white crystalline powder of the product (6.0 g, 12 mmol, 85%). Samples for elemental analysis were additionally purified by repeated crystallization from chloroform/hexanes or column chromatography (silica, hexanes/EtOAc 5:2, $R_f \sim 0.3$). Mp (uncorrected) 217 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.91$ (s, 12H, NMe_2), 7.19 (d, 2H, $^4J_{H,H} = 2.4$ Hz, 4,4′-Ar-H), 7.54 (d, 2H, $^4J_{H,H} = 2.1$ Hz, 6,6′-Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 37.1$ (br s, NMe_2), 127.0 (2,2′-Ar-C), 128.8 (4,4′-Ar-C), 129.7 (6,6′-Ar-C), 135.7 (1,1′-Ar-C), 141.5 (5,5′-Ar-C), 148.2 (3,3′-Ar-C), 163.9 (CO). EI-MS: *m/z* (%) = 498 (0.1) [M^+], 463 (4) [$M^+ - Cl$], 88 (4) [$Me_2NC(S)^+$], 72 (100) [$Me_2NC(O)^+$]. IR (KBr): ν(cm^{-1}) = 1668 (CO, s). Elemental analysis: calcd (%) for $C_{18}H_{16}Cl_4N_2O_2S_2$: C 43.39, H 3.24, N 5.62. Found: C 43.18, H 3.35, N 5.64.

2,2′-Dithio-3,3′,5,5′-tetrachlorobiphenyl (4a). Solid 2,2′-bis-(*N,N*-dimethylcarbamoylthio)-3,3′,5,5′-tetrachlorobiphenyl (**3a**, 2.0 g, 4 mmol) was added in one portion to a stirred suspension of $LiAlH_4$ (1.0 g, 26 mmol) in THF (90 mL) at room temperature, and the resulting reaction mixture refluxed for 12 h. Excess $LiAlH_4$ was destroyed at 0 °C by dropwise addition of degassed water. After hydrogen evolution decreased additional degassed water (30 mL) was added, and the resulting mixture was acidified to pH = 1 with conc. HCl_{aq}. Subsequently all volatiles were removed at 60 °C in vacuum, and the obtained pale yellow residue was extracted with Et_2O (3 × 75 mL) under an atmosphere of dry dinitrogen. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was stirred in boiling EtOH (25 mL) for 20 min and left standing overnight at −20 °C. The precipitate was filtered off and dried in vacuum overnight to afford the product as colorless microcrystalline powder (0.7 g, 2 mmol, 50%). Mp (uncorrected) 154 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.82$ (s, 2H, SH), 7.06 (d, 2H, $^4J_{H,H} = 1.2$ Hz, 4,4′-Ar-H), 7.47 (d, 2H, $^4J_{H,H} = 1.2$ Hz, 6,6′-Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 128.4$ (Ar−C), 129.7 (Ar−C), 131.2 (Ar−C), 131.4 (Ar−C), 133.1 (Ar−C), 139.4 (Ar−C). EI-MS: *m/z* (%) = 354 (33) [M^+], 322 (100) [$M^+ - S$], 286 (72) [$M^+ - SCl$]. IR (KBr): ν(cm^{-1}) = 2577 (SH, m). HRMS (EI): calcd (*m/z*) for $C_{12}H_6Cl_4S_2$: 353.8665. Found: 353.8635.

[(2,2′-Dithio-3,3′,5,5′-tetrachlorobiphenyl)-(4,4′-di-*tert*-butylbipyridine)-zinc]$_{1,2}$ (5a). A solution of dimethylzinc (2.0 M in toluene, 1.86 mL, 3.73 mmol) was added dropwise to a vigorously stirred suspension of 2,2′-dithio-3,3′,5,5′-tetrachlorobiphenyl (**4a**, 1.32 g, 3.73 mmol) in hexanes (20 mL) at room temperature. The reaction mixture was heated to reflux for 20 min to complete methane formation. After cooling to room temperature the white polymeric thiophenolate-zinc species were filtered off, washed with hexanes (2 × 10 mL), and briefly dried in vacuo. This polymeric intermediate was transferred to a Schlenk flask, previously charged with 4,4′-di-*tert*-butylbipyridine (1.0 g, 3.7 mmol), and suspended in benzene (30 mL). The reaction mixture was heated to reflux (oil bath temperature 100 °C) for 1 h, cooled to room temperature, and filtered. The yellowish powder was washed with hexanes (2 × 10 mL) and Et_2O (3 × 20 mL) and subsequently dried in vacuo to afford the pure product (1.4 g, 2.0 mmol, 54%). Mp (uncorrected) 303 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.45$ (s, 18H, 4,4′-^{t}Bu), 7.05 (d, 2H, $^4J_{H,H} = 2.4$ Hz, 4,4′-Ar-H), 7.47 (d, 2H, $^4J_{H,H} = 2.4$ Hz, 6,6′-Ar-H), 7.68 (dd, 2H, $^3J_{H,H} = 5.6$ Hz, $^4J_{H,H} = 1.8$ Hz, 5,5′-Bipy-H), 8.20 (dd, 2H, $^4J_{H,H} = 1.8$ Hz, $^5J_{H,H} = 0.5$ Hz, 3,3′-Bipy-H), 8.40 (d, 2H, $^3J_{H,H} = 5.6$ Hz, 6,6′-Bipy-H). ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 30.4$ (^{t}Bu), 36.1 (CMe_3), 118.9 (3,3′-Bipy-C), 124.7 (5,5′-Bipy-C), 127.8 (6,6′-Ar-C), 127.9 (4,4′-Ar-C), 129.1 (Ar−C), 139.4 (Ar−C), 139.9 (Ar−C), 149.2 (6,6′-Bipy-C), 149.7 (Ar−C), 150.2 (2,2′-Bipy-C), 166.9 (4,4′-Bipy-C). ESI(+)-MS (MeCN): *m/z* (%) = 367 (95) [$BipyZnCl^+$], 639 (100) [$Bipy_2ZnCl^+$], 1055 (22) [$(L)Bipy_2Zn_2Cl^+$]. ESI(−)-MS (MeCN): *m/z* (%) = 455 (100) [$(L)ZnCl^-$]. IR (KBr): ν(cm^{-1}) = 2964 (m), 1615 (s), 1550 (m), 1412 (s), 1368 (s). Elemental analysis: calcd (%) for $C_{60}H_{56}Cl_8N_4S_4Zn_2$: C 52.38, H 4.10, N 4.07, S 9.32. Found: C 52.31, H 4.21, N 4.29, S 7.90. ESI(+)-HRMS (MeCN): calcd (*m/z*) for $C_{30}H_{29}Cl_4N_2S_2Zn$ ($M + H^+$): 684.9812. Found: 684.9811, calcd (*m/z*) for $C_{60}H_{56}Cl_8N_4S_4Zn_2$: 1374.9482. Found: 1374.9474.

2,2′-Bis-(*N,N*-dimethylthiocarbamoyloxy)-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (2b). To a vigorously stirred solution of 3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (**1b**, 8.5 g, 21 mmol) in DMF (70 mL) at 0 °C was added NaH (1.44 g, 60 mmol) in portions during 10 min. After completed addition HMPA (5 mL) was added, and the reaction mixture stirred for 12 h at room temperature. Then dimethylcarbamothioic chloride (10.4 g, 84 mmol) was added in portions, and the resulting mixture was stirred for 3 d at 100 °C. After cooling to room temperature, the reaction was quenched by addition of aqueous KOH solution (3 g KOH in 300 mL of water). The precipitated brown solid was filtered off, dissolved in dichloromethane (150 mL), and washed with water (3 × 100 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated to dryness. The brown oily residue was chromatographed over a silica plug (hexanes/EtOAc 10:1), eluting all spots with $R_f > 0.5$ (TLCs recorded in hexanes/EtOAc 5:1; spots of monosubstituted compound, product and one minor unidentified compound are rather close to each other and were separated only in small scale by elution with hexanes/EtOAc 20:1). The obtained solid pale yellow crude product (containing ∼ 5% monosubstituted compound) was recrystallized from chloroform/hexanes (30 mL/3 mL, reflux to −20 °C) to obtain a white crystalline powder of the pure product (8.0 g, 14 mmol, 65%). Mp (uncorrected) 170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$ (s, 18H, 3,3′-^{t}Bu), 1.37 (s, 18H, 5,5′-^{t}Bu), 2.98 (s, 6H, NMe_2), 3.03 (s, 6H, NMe_2), 7.25 (d, 2H, $^4J_{H,H} = 2.7$ Hz, 6,6′-Ar-H), 7.37 (d, 2H, $^4J_{H,H} = 2.4$ Hz, 4,4′-Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.4$ (3,3′-^{t}Bu), 32.1 (5,5′-^{t}Bu), 34.7 (5,5′-

CMe_3), 35.5 (3,3′-CMe_3), 38.2 (NMe_2), 42.8 (NMe_2), 124.3 (4,4′-Ar-C), 129.3 (6,6′-Ar-C), 132.2 (1,1′-Ar-C), 139.3 (3,3′-Ar-C), 146.8 (5,5′-Ar-C), 147.2 (2,2′-Ar-C), 187.1 (CO). EI-MS: *m/z* (%) = 584 (11) [M^+], 528 (33) [$M^+ - {}^t$Bu], 88 (100) [$Me_2NC(S)^+$], 72 (73) [$Me_2NC(O)^+$]. IR (KBr): ν(cm^{-1}) = 1531 (CS, m). Elemental analysis: calcd (%) for $C_{34}H_{52}N_2O_2S_2$: C 69.82, H 8.96, N 4.79, S 10.96. Found: C 69.57, H 9.02, N 4.84, S 10.97.

2,2′-Bis-(*N,N*-dimethylcarbamoylthio)-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (3b). A 250 mL Schlenk flask was charged with 2,2′-bis-(*N,N*-dimethylthiocarbamoyloxy)-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (**2b**, 7.0 g, 12 mmol) and heated to 320 °C without agitation for 4 h. The resulting dark orange oil was dissolved in a minimum amount of dichloromethane and purified by column chromatography (silica, hexanes/EtOAc 10:1, TLCs recorded in hexanes/EtOAc 5:1, $R_f \sim 0.5$) to obtain a white powder of the product (5.0 g, 8.5 mmol, 71%). Mp (uncorrected) 206 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (s, 18H, 3,3′-^{t}Bu), 1.50 (s, 18H, 5,5′-^{t}Bu), 2.65 (br s, 12H, NMe_2), 3.03 (s, 6H, NMe_2), 7.12 (br s, 2H, 6,6′-Ar-H), 7.44 (d, 2H, $^4J_{H,H}$ = 2.5 Hz, 4,4′-Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.3 (^{t}Bu), 31.5 (^{t}Bu), 34.9 (CMe_3), 36.8 (br s, NMe_2) 37.1 (CMe_3), 122.7 (4,4′-Ar-C), 123.3 (6,6′-Ar-C), 126.3 (1,1′-Ar-C), 150.6 (3,3′-Ar-C), 151.1 (5,5′-Ar-C), 152.2 (2,2′-Ar-C), 167.1 (CO). EI-MS: *m/z* (%) = 584 (12) [M^+], 528 (32) [$M^+ - {}^t$Bu], 88 (100) [$Me_2NC(S)^+$], 72 (63) [$Me_2NC(O)^+$]. IR (KBr): ν(cm^{-1}) = 1669 (CO, m). Elemental analysis: calcd (%) for $C_{34}H_{52}N_2O_2S_2$: C 69.82, H 8.96, N 4.79, S 10.96. Found: C 69.85, H 9.02, N 4.70, S 11.00.

2,2′-Dithio-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (4b). A solution of 2,2′-bis-(*N,N*-dimethylcarbamoylthio)-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (**3b**, 2.0 g, 3.4 mmol) in THF (50 mL) was added dropwise during 1 h to a suspension of $LiAlH_4$ (0.65 g, 17 mmol) in THF (30 mL) at 0 °C and then refluxed for 3 h. The resulting reaction mixture was stirred overnight at room temperature, cooled to 0 °C, and carefully quenched by dropwise addition of degassed water. After hydrogen evolution decreased additional degassed water (30 mL) was added, and the resulting mixture was acidified to pH = 1 with diluted HCl_{aq}.(~ 12%) The reaction mixture was extracted with Et_2O (3 × 100 mL) under an atmosphere of dry dinitrogen. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was stirred in boiling EtOH (30 mL) for 20 min and left standing overnight at 4 °C. The precipitate was filtered off and dried in vacuum overnight to afford the product as a white powder (0.8 g, 1.8 mmol, 52%). Mp (uncorrected) 173 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (s, 18H, 3,3′-^{t}Bu), 1.55 (s, 18H, 5,5′-^{t}Bu), 3.47 (s, 2H, SH), 7.06 (d, 2H, $^4J_{H,H}$ = 2.5 Hz, 2H, 6,6′-Ar-H), 7.48 (d, 2H, $^4J_{H,H}$ = 2.0 Hz, 4,4′-Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.1 (3,3′-^{t}Bu), 31.4 (5,5′-^{t}Bu), 34.7 (5,5′-CMe_3), 36.8 (3,3′-CMe_3), 123.6 (4,4′-Ar-C), 125.2 (6,6′-Ar-C), 127.8 (1,1′-Ar-C), 142.2 (3,3′-Ar-C), 147.2 (5,5′-Ar-C), 148.0 (2,2′-Ar-C). EI-MS: *m/z* (%) = 442 (3) [M^+], 409 (16) [M^+ − S], 393 (10) [M^+ − SMe], 353 (9) [M^+ − S^{t}Bu], 57 (100) [^{t}Bu$^+$]. IR (KBr): ν(cm^{-1}) = 2569 (SH, m). HRMS (EI): calcd (*m/z*) for $C_{28}H_{42}S_2$: 442.2728. Found: 442.2722.

(2,2′-Dithio-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl)-(4,4′-di-*tert*-butylbipyridine)-zinc (5b). A solution of dimethylzinc (2.0 M in toluene, 0.62 mL, 1.24 mmol) was added dropwise to a stirred solution of 2,2′-dithio-3,3′,5,5′-tetrakis-*tert*-butylbiphenyl (**4b**, 0.55 g, 1.24 mmol) in hexanes (10 mL) at room temperature and stirring was continued for 1 h. The turbid viscous reaction mixture was condensed to dryness and redissolved in toluene (15 mL). Solid 4,4′-di-*tert*-butylbipyridine (0.33 g, 1.24 mmol) was added, and the reaction mixture stirred for 10 min to afford a clear orange solution. The solvent was reduced to half of its volume, and pentane (10 mL) was added to precipitate a fine yellow powder. It was filtered off, washed with pentane (2 × 10 mL), and dried in vacuo overnight to afford the yellowish product (0.55 g, 0.71 mmol, 57%) largely free of residual solvents. Mp (uncorrected) 281 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.86 (s, 18H, 3,3′-^{t}Bu), 1.45 (s, 18H, 4,4′-^{t}Bu), 2.03 (s, 18H, 5,5′-^{t}Bu), 6.10 (dd, 2H, $^3J_{H,H}$ = 5.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 5,5′-Bipy-H), 7.15 (d, approximately 2H - overlapping with C_6D_6, $^4J_{H,H}$ = 2.5 Hz, 6,6′-Ar-H), 7.34 (d, 2H, $^4J_{H,H}$ = 1.5 Hz, 3,3′-Bipy-H), 7.57 (d, 2H, $^4J_{H,H}$ = 2.5 Hz, 4,4′-Ar-H), 7.84 (d, 2H, $^3J_{H,H}$ = 6.0 Hz, 6,6′-Bipy-H). ^{13}C NMR (125 MHz, C_6D_6): δ = 29.8 (3,3′-^{t}Bu), 31.3 (5,5′-^{t}Bu), 32.0 (4,4′-^{t}Bu), 34.8 (3,3′-CMe_3), 34.9 (5,5′-CMe_3), 38.2 (4,4′-CMe_3), 117.2 (6,6′-Bipy-C), 121.4 (Ar−C), 123.0 (3,3′-Bipy-C), 126.2 (6,6′-Ar-C), 128.3 (5,5′-Bipy-C), 137.3 (Ar−C), 145.1 (Ar−C), 149.3 (Ar−C), 149.7 (4,4′-Ar-C), 154.2 (2,2′-Bipy-C), 166.9 (4,4′-Bipy-C). ESI(+)-MS (MeCN): *m/z* (%) = 773 (100) [MNa^+], 1571 (35) [M_2Na^+]. IR (KBr): ν(cm^{-1}) = 2961 (s), 2905 (m), 1615 (s), 1550 (w), 1409 (m). Elemental analysis: calcd (%) for $C_{64}H_{64}N_2S_2Zn$: C 71.38, H 8.33, N 3.62, S 8.28. Found: C 70.43, H 8.23, N 3.30, S 7.35. ESI(+)-HRMS (MeCN): calcd (*m/z*) for $C_{64}H_{65}N_2S_2Zn$ (M + H^+): 773.3875. Found: 773.3870.

3,3′-Diallyl-2,2′-bis-(*N,N*-dimethylthiocarbamoyloxy)-biphenyl (2c). A solution of 3,3′-diallyl-2,2′-dihydroxybiphenyl (**1c**, 12.3 g, 45.2 mmol) in DMF (120 mL) was treated with sodium hydride (2.48 g, 103 mmol) in portions at 0 °C and stirred for 2 h. Dimethylcarbamothioic chloride (13.3 g, 108 mmol) was added in portions, and the suspension was stirred at 90 °C for 4 h. After cooling to room temperature the reaction mixture was treated with aqueous KOH (1%, 500 mL) and extracted with CH_2Cl_2 (500 mL). The organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated to dryness. The resulting brown oil was purified via column chromatography (silica, hexanes/CH_2Cl_2 1:3, $R_f \sim 0.5$) to afford the product as a white solid (6.5 g, 15 mmol, 32%). Mp (uncorrected) 99 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.97 (s, 4H, NMe_2), 2.98 (s, 2H, NMe_2), 3.16 (*s*, 4H, NMe_2), 3.22 (br s, 2H, NMe_2), 3.27−3.45 (m, 4H, CH_2), 5.04 (m, 2H, CH=CHH_{trans}), 5.06 (dq, $^3J_{H,H}$ = 10.5 Hz, $^2J_{H,H}$ = 1.5 Hz, 2H, CH=CH_{cis}H), 5.95 (ddt, $^3J_{H,H}$ = 17.1, 10.5, 6.3 Hz, 2H, C*H*=CH_2), 7.14−7.24 (m, 6H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.0 (CH_2), 35.1 (CH_2), 38.0 (NMe_2), 43.0 (NMe_2), 115.9 (CH=*C*H_2), 124.9 (Ar−C), 125.9 (Ar−C), 129.5 (Ar−C), 129.6 (Ar−C), 130.1 (Ar−C), 131.7 (Ar−C), 132.7 (Ar−C), 136.3 (*C*H=CH_2), 136.5 (*C*H=CH_2), 149.5 (Ar−C), 149.8 (Ar−C), 186.4 (CS). EI-MS: *m/z* (%) = 440 (70) [M^+], 425 (5) [$M^+ - CH_3$], 368 (100) [$M^+ - C(O)N(CH_3)_2$], 352 (40) [$M^+ - C(S)N(CH_3)_2$], 336 (40) [$M^+ - OC(S)N(CH_3)_2$], 264 (45) [$M^+ - 2\ C(S)N(CH_3)_2$]. IR (KBr): ν(cm^{-1}) = 1535 (CS, s). Elemental analysis: calcd (%) for $C_{24}H_{28}N_2O_2S_2$: C 65.42, H 6.41, N 6.36. Found: C 66.33, H 6.34, N 6.21.

3,3′-Diallyl-2,2′-bis-(*N,N*-dimethylcarbamoylthio)-biphenyl (3c). A 250 mL Schlenk flask was charged with 3,3′-diallyl-2,2′-bis-(*N,N*-dimethylthiocarbamoyloxy)-biphenyl (**2c**, 2.8 g, 6.4 mmol) and heated to 320 °C for 1 h without agitation. The resulting brown oil was cooled to room temperature and purified by column chromatography (silica, hexanes/EtOAc 5:1, $R_f \sim 0.2$) to yield the product as a colorless solid (1.5 g, 3.4 mmol, 54%). Mp (uncorrected) 114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.81 (s, 12H, NMe_2), 3.56 (dd, $^2J_{H,H}$ = 16.0 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, CH_2), 3.66 (dd, $^2J_{H,H}$ = 16.0 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, CH_2), 5.02 (dq, $^3J_{H,H}$ = 17.0 Hz, $^2J_{H,H}$ = 2.0 Hz, 2H, CH=CHH_{trans}), 5.06 (dq, $^3J_{H,H}$ = 10.0 Hz, $^2J_{H,H}$ = 1.5 Hz, 2H, CH=CH_{cis}H), 6.01 (ddt, $^3J_{H,H}$ = 17.0, 10.0, 6.5 Hz, 2H, C*H*=CH_2), 7.11 (d, $^3J_{H,H}$ = 2 Hz, Ar−H), 7.13 (d, $^3J_{H,H}$ = 2 Hz, Ar−H), 7.26−7.32 (m, 4H, Ar−H). ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 36.9 (NMe_2), 39.1 (CH_2), 115.8 (CH=*C*H_2), 127.7 (Ar−C), 128.7 (Ar−C), 128.8 (Ar−C), 129.0 (Ar−C), 137.4 (*C*H=CH_2), 144.8 (Ar−C), 148.2 (Ar−C), 166.2 (CO). EI-MS: *m/z* (%) = 440 (50) [M^+], 368 (70) [M^+ − C(O)N(CH_3)$_2$], 336 (100) [M^+ − SC(O)N(CH_3)$_2$], 295 (30) [M^+ − 2 C(O)N(CH_3)$_2$ − H], 264 (90) [M^+ − C(O)N(CH_3)$_2$ − SC(O)N(CH_3)$_2$]. IR (KBr): ν(cm^{-1}) = 1661 (CO, s). Elemental analysis: calcd (%) for $C_{24}H_{28}N_2O_2S_2$: C 65.42, H 6.41, N 6.36. Found: C 65.33, H 6.36, N 6.18.

3,3′-Diallyl-2,2′-dithiobiphenyl (4c). To a suspension of $LiAlH_4$ (1.90 g, 50.1 mmol) in THF (80 mL) was slowly added a solution of 3,3′-diallyl-2,2′-bis-(*N,N*-dimethylcarbamoylthio)-biphenyl (**3c**, 6.90 g, 15.7 mmol) in THF (60 mL), and the reaction mixture was refluxed for 3 h. After cooling to 0 °C degassed water was carefully added to destroy excess $LiAlH_4$, and the mixture was neutralized with degassed aqueous NH_4Cl solution (200 mL). The mixture was extracted with Et_2O (3 × 100 mL). The combined organic phases were dried over Na_2SO_4, filtered, and evaporated to give the product as a pale yellow oil (2.94 g, 9.85 mmol, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.25 (s, 2H, SH), 3.50 (d, $^3J_{H,H}$ = 5.0 Hz, 4H, CH_2), 5.13 (m, 4H, CH=C*H*$_2$), 6.01 (ddt, $^3J_{H,H}$ = 20.8, 13.3, 3.7 Hz, 2H, C*H*=CH_2), 7.03−7.24 (m, 6H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.1 (CH_2), 116.8 (CH=*C*H_2), 125.4 (Ar−C), 128.2 (Ar−C), 129.2 (Ar−C), 131.8 (Ar−C), 135.3 (*C*H=CH_2), 138.1 (Ar−C), 140.2 (Ar−C). EI-MS: *m/z* (%) = 298 (100) [M^+], 265 (30) [M^+ − SH]. IR (KBr): ν(cm^{-1}) = 2576 (SH, m). HRMS (EI): calcd (*m/z*) for $C_{18}H_{18}S_2$: 298.0850. Found: 298.0854.

(3,3′-Diallylbiphenyl-2,2′-dithio)-(4,4′-di-*tert*-butylbipyridine)-zinc (5c). To a solution of 4,4′-di-*tert*-butylbipyridine (0.50 g, 1.85 mmol) in toluene (10 mL) was slowly added dimethylzinc (2.0 M in toluene, 0.93 mL, 1.85 mmol) at −78 °C yielding a yellow suspension. After 10 min, a solution of 3,3′-diallyl-2,2′-dithiobiphenyl (**4c**, 0.55 g, 1.85 mmol) in toluene (5 mL) was added. Warming to room temperature yielded a yellow solution which was evaporated to dryness. The residue was dissolved in a minimal amount of CCl_4 and layered with pentane (10 mL). The resulting yellow powder was filtered off, washed with pentane (2 × 10 mL), and dried in vacuo overnight to afford the product (0.50 g, 0.79 mmol, 43%). Despite repeated recrystallization, no satisfying elemental analysis could be obtained although the composition is confirmed by HRMS. Mp (uncorrected) 125 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.44 (s, 18H, 4,4′-^{t}Bu), 3.58 (dd, $^2J_{H,H}$ = 15.5 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, C*H*$_2$), 3.70 (dd, $^2J_{H,H}$ = 15.5 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, C*H*$_2$), 4.95 (m, 2H, CH=C*H*$_2$), 5.02 (m, 2H, CH=C*H*$_2$), 6.06 (ddt, $^3J_{H,H}$ = 16.5, 10.0, 6.5 Hz, 2H, C*H*=CH_2), 6.96 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 2H, 6,6′-Ar-H), 7.09 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, 5,5′-Ar-H), 7.16 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 2H, 4,4′-Ar-H), 7.58 (dd, 2H, $^3J_{H,H}$ = 5.5 Hz, $^4J_{H,H}$ = 1.0 Hz, 5,5′-Bipy-H), 8.10 (d, 2H, $^3J_{H,H}$ = 5.5 Hz, 6,6′-Bipy-H), 8.18 (d, 2H, $^4J_{H,H}$ = 1.0 Hz, 3,3′-Bipy-H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 30.5 (^{t}Bu), 36.0 (CMe_3), 40.9 (CH_2), 114.9 (CH=*C*H_2), 118.6 (3,3′-Bipy-C), 123.6 (5,5′-Ar-C), 124.3 (5,5′-Bipy-C), 127.1 (4,4′-Ar-C), 128.0 (6,6′-Ar-C), 138.7 (*C*H=CH_2), 140.2 (Ar−C), 142.8 (Ar−C), 149.3 (Ar−C), 149.7 (Ar−C), 150.0 (2,2′-Bipy-C), 166.3 (4,4′-Bipy-C). ESI(+)-MS (MeCN): *m/z* (%) = 630 (100) [M^+], 1260 (100) [M_2^+]. IR (KBr): ν(cm^{-1}) = 3050 (m), 2966 (s), 2905 (m), 2871 (m), 1614 (s), 1549 (m), 1410 (m). ESI(+)-HRMS (MeCN): calcd (*m/z*) for $C_{36}H_{41}N_2S_2Zn$ (M + H^+): 629.1997. Found: 629.1998.

(3,3′-Diallylbiphenyl-2,2′-dithio)-(diphenyl)-tin (6c). A solution of 3,3′-diallyl-2,2′-dithiobiphenyl (**4c**, 0.3 g, 1.0 mmol) and diphenyltindichlorid (0.34 g, 1.0 mmol) in THF (10 mL) was cooled to 0 °C and treated with triethylamine (0.15 mL, 0.11 g, 1.1 mmol). After 1 h, Et_2O (20 mL) was added and a white precipitate (triethylammonium chloride) was removed by filtration. Removal of the solvents in vacuo yielded **6c** as a colorless solid. Large single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a THF solution of the complex. Mp 60 °C (decomposition). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.26 (dd, $^2J_{H,H}$ = 15.5 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, C*H*$_2$), 3.57 (dd, $^2J_{H,H}$ = 15.5 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, C*H*$_2$), 4.88−4.84 (m, 4H, CH=C*H*$_2$), 5.72 (ddt, $^3J_{H,H}$ = 16.5, 10.0, 6.5 Hz, 2H, C*H*=CH_2), 7.12 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 2H, Ar−H), 7.17 (dd,, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 2H, Ar−H), 7.29 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, Ar−H), 7.33−7.42 (m, 10H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.7 (CH_2), 116.0 (CH=*C*H_2), 127.5 (Ar−C), 127.7 (Ar−C), 128.4 (Ar−C), 129.0 (Ar−C), 129.6 (Ar−C), 130.5 (Ar−C), 136.0 (Ar−C), 136.7 (*C*H=CH_2), 137.9 (Ar−C), 144.4 (Ar−C), 149.3 (Ar−C). ^{119}Sn NMR (187 MHz, $CDCl_3$): δ = 42.4. EI-MS: *m/z* (%) = 570 (10) [M^+]. IR (KBr): ν(cm^{-1}) = 3045 (br), 2970 (br), 1450 (m), 1430 (s), 1395 (m), 774 (m), 730 (s), 695 (m). HRMS (ESI): calcd (*m/z*) for $C_{30}H_{27}S_2Sn$ (M + H): 571.0573. Found: 571.0571.

O,O′−2,2′-Methylenebis-(2,1-phenylene)-bis-(dimethylcarbamothioate) (2d). To a stirred solution of 2,2′-methylenediphenol (**1d**, 12.5 g, 62 mmol) in DMF (175 mL) was added NaH (4.25 g, 177 mmol) in portions during 15 min. HMPA (25 mL) was then added, and the reaction mixture stirred at room temperature for 2.5 h. Dimethylcarbamothioic chloride (27.0 g, 220 mmol) was then added in one portion, and the resulting yellow suspension stirred at 80−85 °C for 36 h. The resulting reaction mixture was cooled to room temperature, quenched with water (1 L), and extracted with a mixture of chloroform and pentane (4:1(v:v), 4 × 200 mL). The combined organic phases were washed with aqueous NaOH (10%, 2 × 100 mL) and brine (200 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The resulting brown liquid was treated with methanol (250 mL) causing the crude product to precipitate as a yellow powder. It was filtered off and recrystallized from methanol (200 mL, reflux to +4 °C) to afford the product as a white crystalline powder (17.1 g, 46 mmol, 74%). Mp (uncorrected) 163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.08 (s, 6H, NMe_2), 3.39 (s, 6H, NMe_2), 3.85 (s, 2H, CH_2), 7.01 (dd, 2H, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.3 Hz, 6,6′-Ar-H), 7.08 (dd, 2H, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.9 Hz, 3,3′-Ar-H), 7.15 (dt, 2H, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.3 Hz, 4,4′-Ar-H), 7.26 (dt, 2H, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.9 Hz, 5,5′-Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.4 (NMe_2), 38.5 (CH_2), 43.2 (NMe_2), 123.3 (Ar−C), 126.1 (Ar−C), 127.4 (Ar−C), 130.5 (Ar−C), 132.5 (Ar−C), 152.3 (Ar−C), 186.7 (CS). EI-MS: *m/z* (%) = 374 (10) [M^+], 270 (25) [M^+ − $Me_2NC(O)S$], 197 (20) [M^+ − $Me_2NC(O)SC(O)NMe_2$], 88 (100) [Me_2NCS^+], 72 (40) [$Me_2NC(O)^+$]. IR (KBr): ν(cm^{-1}) = 1535 (CS, s). Elemental analysis: calcd (%) for $C_{19}H_{22}N_2O_2S_2$: C 60.93, H 5.92, N 7.48, S 17.12. Found: C 60.68, H 5.88, N 7.34, S 16.87.

***S,S′*-2,2′-Methylenebis-(2,1-phenylene)-bis-(dimethylcarbamothioate) (3d).** A 250 mL Schlenk flask was charged with *O,O′*-2,2′-methylenebis-(2,1-phenylene)-bis-(dimethylcarbamothioate) (**2d**, 8.0 g, 21 mmol) and heated to 310 °C without agitation for 45 min. The resulting yellow oil was cooled to room temperature and purified by column chromatography (silica, CH_2Cl_2/EtOAc 20:1, R_f ~ 0.25). The pale yellow product was dried at 120 °C/10^{-3} mbar for 4 h to remove remaining EtOAc; the product solidified after standing for several days at room temperature and was ground in a mortar to afford a fine yellow powder of the pure product (5.2 g, 14 mmol, 65%). Mp (uncorrected) 76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00 (br s, 12H, NMe_2), 4.31 (s, 2H, CH_2), 7.05 (dd, 2H, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.7 Hz, 3,3′-Ar-H), 7.20 (dt, 2H, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.7 Hz, 4,4′-Ar-H), 7.27 (dt, 2H, $^3J_{H,H}$ = 7.5

Hz, $^4J_{H,H}$ = 1.7 Hz, 5,5′-Ar-H), 7.50 (dd, 2H, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.7 Hz, 6,6′-Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.9 (NMe_2), 38.3 (CH_2), 126.8 (Ar−C), 128.4 (Ar−C), 130.0 (Ar−C), 130.6 (Ar−C), 137.5 (Ar−C), 145.3 (Ar−C), 166.5 (CO). EI-MS: *m/z* (%) = 374 (15) [M^+], 270 (25) [$M^+ - Me_2NC(O)S$], 197 (35) [$M^+ - Me_2NC(O)SC(O)NMe_2$], 72 (100) [$Me_2NC(O)^+$]. IR (KBr): ν(cm^{-1}) = 1670 (CO, s). Elemental analysis: calcd (%) for $C_{19}H_{22}N_2O_2S_2$: C 60.93, H 5.92, N 7.48, S 17.12. Found: C 60.62, H 5.76, N 7.42, S 16.98.

2,2′-Methylenedibenzenethiol (4d). A solution of *S,S'*-2,2′-methylenebis-(2,1-phenylene)-bis-(dimethylcarbamothioate) (**3d**, 4.8 g, 13 mmol) in 60 mL THF was slowly added to a suspension of $LiAlH_4$ (2.4 g, 63 mmol) in 120 mL THF and heated to reflux for 24 h. The resulting reaction mixture was cooled to 0 °C, and excess $LiAlH_4$ was destroyed by dropwise addition of degassed water. After hydrogen evolution decreased additional degassed water (180 mL) was added, and the resulting mixture was acidified to pH = 1 with conc. HCl_{aq}. The reaction mixture was extracted with Et_2O (4 × 120 mL) under an atmosphere of dry dinitrogen. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was taken up in boiling hexanes (30 mL) and filtered through dry celite. After washing the celite pad with hot hexanes (30 mL) all volatiles were removed in vacuum to afford the product as a colorless microcrystalline powder (2.0 g, 8.6 mmol, 66%). Mp (uncorrected) 57 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.33 (s, 2H, SH), 4.05 (s, 2H, CH_2), 6.93 (dd, 2H, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.9 Hz, 3,3′-Ar-H), 7.09−7.12 (m, 4H, 4,4′-Ar-H, 5,5′-Ar-H), 7.35 (dd, 2H, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.9 Hz, 6,6′-Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.0 (CH_2), 126.3 (Ar−C), 127.2 (Ar−C), 129.9 (Ar−C), 130.9 (Ar−C), 131.2 (Ar−C), 137.4 (Ar−C). EI-MS: *m/z* (%) = 232 (55) [M^+], 197 (100) [$M^+ - H_2S$]. IR (KBr): ν(cm^{-1}) = 2563 (SH, m). HRMS (EI): calcd (*m/z*) for $C_{13}H_{12}S_2$: 232.0380. Found: 232.0379.

Bis-[(2,2′-methylenedibenzenethio)-(4,4′-di-*tert*-butylbipyridine)-zinc] (5d). A solution of dimethylzinc (2.0 M in toluene, 1.0 mL, 2.0 mmol) was added dropwise to a vigorously stirred suspension of 2,2′-methylenedibenzenethiol (**4d**, 0.46 g, 2.0 mmol) in hexanes (10 mL) at room temperature. The reaction mixture was heated to reflux for 20 min to complete methane formation. After cooling to room temperature the white polymeric thiophenolate-zinc species were filtered off, washed with hexanes (2 × 5 mL), and briefly dried in vacuo. This polymeric intermediate was transferred to a Schlenk flask, previously charged with 4,4′-di-*tert*-butylbipyridine (0.54 g, 2.0 mmol) and suspended in benzene (15 mL). The reaction mixture was heated to reflux (oil bath temperature 100 °C) for 1 h, cooled to approximately 45 °C, and filtered. The yellowish powder was washed with benzene (2 × 5 mL) and dried in vacuo to afford the pure product (0.70 g, 1.2 mmol, 62%). Mp (uncorrected) 292 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.44 (s, 36H, 4,4′-^{t}Bu), 4.47 (s, 4H, CH_2), 6.74 (m, 4H, 4,4′-Ar-H), 6.80 (m, 4H, 5,5′-Ar-H), 7.87 (m, 4H, 3,3′-Ar-H), 7.22 (d, 4H, $^3J_{H,H}$ = 7.5 Hz, 6,6′-Ar-H), 7.60 (dd, 4H, $^3J_{H,H}$ = 5.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 5,5′-Bipy-H), 8.06 (s, 4H, 3,3′-Bipy-H), 8.69 (d, 4H, $^3J_{H,H}$ = 5.5 Hz, 6,6′-Bipy-H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 30.5 (^{t}Bu), 35.9 (CMe_3), 41.9 (CH_2), 118.4 (3,3′-Bipy-C), 123.4 (5,5′-Ar-C), 124.4 (5,5′-Bipy-C), 125.5 (4,4′-Ar-C), 129.8 (3,3′-Ar-C), 134.9 (6,6′-Ar-C), 142.1 (Ar−C), 142.3 (Ar−C), 149.5 (6,6′-Bipy-C), 149.7 (2,2′-Bipy-C), 165.7 (4,4′-Bipy-C). ESI(+)-MS (MeCN): *m/z* (%) = 291 (100) [$BipyNa^+$], 1151 (9) [MNa^+]. ESI(−)-MS (MeCN): *m/z* (%) = 331 (100) [$(4d)ZnCl^-$]. IR (KBr): ν(cm^{-1}) = 2961 (s), 1615 (s), 1410 (m), 1391 (m). Elemental analysis: calcd (%) for $C_{62}H_{68}N_4S_4Zn_2$: C 66.00, H 6.07, N 4.97, S 11.37. Found: C 64.95, H 5.89, N 4.87, S 11.22. ESI(+)-HRMS (MeCN): calcd (*m/z*) for $C_{62}H_{69}N_4S_4Zn_2$ ($M + H^+$): 1125.29825. Found: 1125.29754.

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Supporting Information Available: Additional experimental procedures and compound characterization data. ^{1}H and ^{13}C NMR spectra for all new compounds and DOSY-NMR spectra for **4a**, **4b**, **4c**, **4d**, **5a**, **5b**, **5c**, and **5d**. Complete crystallographic data and crystallographic information files (CIFs) for **4a**, **5a**, **5b**, **5d**, and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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