1617, $\lambda = 71.069$ pm, $T = 293$ K, $\mu(Mo_{K\alpha}) = 0.462$ mm^{-1}, crystal dimensions $0.4 \times 0.3 \times 0.25$ mm^3, $2 \le 2\theta \le 50^\circ$; of 7153 measured reflections, 6525 were unique; 462 parameters refined in full matrix, $R1 = 0.039$ with 3411 reflections ($I > 3\sigma(I)$), $wR2 = 0.041$, $w = 1$, min./max. residual electron density $-290/480$ e nm^{-3}. (Ph_4P)-**4**: $C_{42}H_{35}O_6PSiW$, $M_r = 878.644$, monoclinic, space group $P2_1/c$ (no. 14); $a = 1089.2(2)$, $b = 1744.0(4)$, $c = 1989.7(3)$ pm, $\beta = 100.05(1)^\circ$, $V = 3.722(2)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.57$ Mg m^{-3}, $F(000) = 1747$, $\lambda = 71.069$ pm, $T = 293$ K, $\mu(Mo_{K\alpha}) = 3.29$ mm^{-1}, crystal dimensions $0.25 \times 0.25 \times 0.15$ mm^3, $2 \le 2\theta \le 56^\circ$; of 7144 measured reflections, 6519 were unique; 462 parameters refined in full matrix, $R1 = 0.032$ with 4031 reflections ($I > 3\sigma(I)$), $wR2 = 0.037$, $w = 1$, min./max. residual electron density $-910/790$ e nm^{-3}. (Ph_4P)$_2$-**5**: $C_{72}H_{60}O_{13}P_2Si_2Mo_2$, $M_r = 1443.261$, monoclinic, space group $P2_1/c$ (no. 14); $a = 1305.0(2)$, $b = 1560.2(3)$, $c = 1676.9(6)$ pm, $\beta = 103.90(2)^\circ$, $V = 3.314(1)$ nm^3, $Z = 2$, $\rho_{calcd} = 1.45$ Mg m^{-3}, $F(000) = 1469$, $\lambda = 71.069$ pm, $T = 293$ K, $\mu(Mo_{K\alpha}) = 1.025$ mm^{-1}, crystal dimensions $0.5 \times 0.6 \times 0.2$ mm^3, $2 \le 2\theta \le 56^\circ$; of 8624 measured reflections, 7973 were unique; 503 parameters refined in full matrix, $R1 = 0.045$ with 4724 reflections ($I > 3\sigma(I)$) and $wR2 = 0.047$, $w = 1$, min./max. residual electron density $-640/870$ e nm^{-3}. The data were collected on a Enraf-Nonius CAD4 four circle diffractometer (ω-2θ scans). All measurements were made at room temperature; two standard reflections showed no significant variation in intensity. Corrections were made for Lorentzian and polarization effects; an extinction correction was also applied;[19] an empirical absorption correction on the basis of Ψ scan data was introduced. The structures were solved by direct methods (SHELXS-86 program)[20] and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found on difference Fourier maps; their positions were not refined and they were given one overall isotropic thermal parameter. Refinements were carried out by minimizing the function $\Sigma w(|F_O| - |F_C|)^2$, where F_O and F_C are the observed and calculated structure factors (program CRYSTALS).[21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100828. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Solution and Solid-State Studies of a Chiral Zinc–Sulfonamide Complex Relevant to Enantioselective Cyclopropanations**

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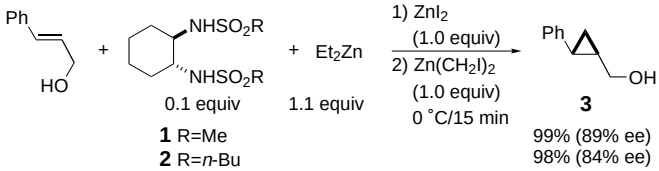
Sulfonamide derivatives of chiral amines and diamines have recently emerged as an important class of auxiliaries and catalysts in enantioselective transformations.[1] Chiral sulfonamides serve admirably as ligands for a number of different metals and have been employed in a wide variety of synthetically useful reactions, for example, cyclopropanation (Zn),[2] addition of dialkylzinc to aldehydes (Ti),[3–6] Mukaiyama aldol reaction (lanthanides),[7] enantiotopic group differentiation (Li),[8] Diels–Alder reactions (Al),[9] and enantioselective allylation of aldehydes (B).[10] In each of these systems, it is generally assumed that the metal is covalently bound to sulfonamide nitrogen atoms. Indeed, Corey et al. have provided an X-ray crystal structure of a chiral diazaaluminolidine prepared from *N,N*′-(1,2-diphenylethylene)bis(trifluoromethanesulfonamide) and trimethylaluminum, which clearly shows that the aluminum atom is bound in just such a manner.[11] Our interest in this area derives from the demonstration that chiral bis(sulfonamide)s which, when pretreated with diethylzinc, are effective catalysts for the enantioselective cyclopropanation of allylic alcohols.[12] Herein we provide reaction data, elemental analyses, spectroscopy studies, and an X-ray crystal structure in support of a catalyst structure which, among other interesting features, contains a zinc atom bound to both sulfonamide nitrogen atoms.

Although our previous studies have shown (*R,R*)-*N,N*′-cyclohexane-1,2-diyl)bis(methanesulfonamide) (**1**) to be the optimal cyclopropanation catalyst (Scheme 1), we selected the analogous and equipotent bis(*n*-butanesulfonamide) **2** for these structural studies owing to its superior solubility (e.g. in CH_2Cl_2: **1**: ≈ 1 mg mL^{-1} CH_2Cl_2; **2**: > 40 mg mL^{-1}).

We first established the chemical composition of the catalyst, which according to earlier studies requires the combination of **1** with diethylzinc.[12c] Therefore, a solution of **2** in dichloromethane was treated with diethylzinc (1.0 equiv, room temperature), and the solvent removed in



Scheme 1. Bis(sulfonamide)-catalyzed enantioselective cyclopropanation.

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vacuo. The resulting off-white powder provided a correct elemental analysis (C, H, N, S, Zn)[13] for the formula $C_{14}H_{28}N_2O_4S_2Zn$, which corresponds to the simple zinc salt of **2** (i.e., $[Zn^{2+}(\mathbf{2}-2H)^{2-}]$). That deprotonation at the sulfonamide nitrogen atom had occurred was confirmed by ^{1}H NMR spectroscopy. A comparison of the spectra acquired before and after the addition of diethylzinc (1.0 equiv) to **2** in $CDCl_3$ showed clearly that the sulfonamide NH protons ($\delta =$ 4.78) had disappeared (Figure 1a and b). Interestingly, the

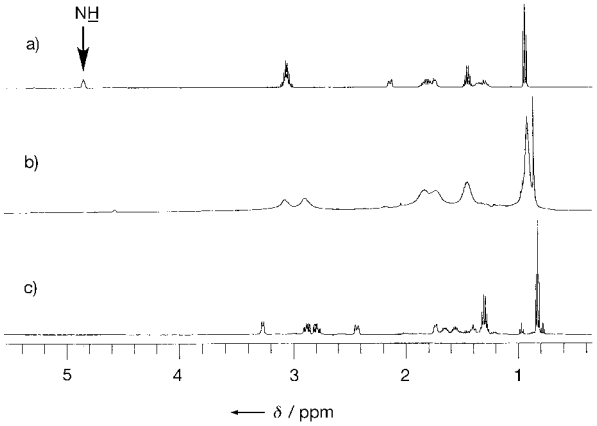
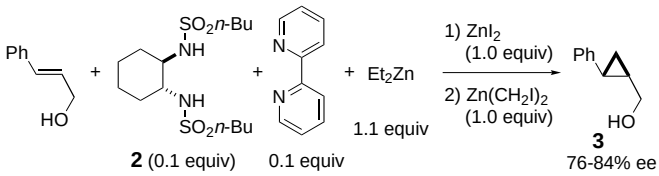


Figure 1. ^{1}H NMR spectra of a) **2**, b) **2** + Et_2Zn (1.0 equiv), c) **2** + Et_2Zn (1.0 equiv) + bipy (1.0 equiv).

remaining signals became very broad, which suggested that the zinc–sulfonamide species was aggregated. Furthermore, the solution had gelled within 15 min of the addition of diethylzinc, thus providing additional evidence that the zinc–sulfonamide species was strongly self-associating. The gel could be solubilized by the addition of pyridine (2 equiv), 1,10-phenanthroline (1 equiv), or 2,2′-bipyridyl (bipy, 1 equiv). The ^{1}H NMR spectrum of $[Zn^{2+}(\mathbf{2}-2H)^{2-}]$ which had been treated with one equivalent of bipy displayed very sharp resonances (Figure 1c). Presumably, the bidentate ligand was capable of disrupting the intermolecular zinc–sulfonamide interactions to give a monomeric complex.

Having demonstrated that deprotonation of **2** to form a zinc complex proceeds efficiently under the chosen reaction conditions, we next sought to establish that $[Zn^{2+}(\mathbf{2}-2H)^{2-}]$ is a kinetically significant species. Therefore, the zinc–sulfonamide complex was formed from **2** (0.1 equiv) and diethylzinc (0.1 equiv) under the same conditions as for the NMR experiment, and this solution was then added to ethylzinc cinnamyl alcoholate followed by the addition of zinc iodide (1.0 equiv) and di(iodomethyl)zinc (1.0 equiv). The product cyclopropane **3** was formed rapidly with 83% *ee*. This verified that the active form of the sulfonamide must be the deprotonated species produced upon treatment of **2** with diethylzinc.

In addition, we also demonstrated that the zinc–sulfonamide moiety remains intact and catalytically active upon complexation with bipy. Two different protocols were used to generate this species (Scheme 2). In the first reaction, all three components (cinnamyl alcohol, **2**, and bipy) were combined prior to treatment with diethylzinc. The product was obtained with the same selectivity (84% *ee*) as in the absence of bipy (see Scheme 1). In the second reaction, $[Zn^{2+}(\mathbf{2}-2H)^{2-}]$



Scheme 2. Cyclopropanation with **2** in the presence of bipy.

(0.1 equiv) was formed separately and then treated with bipy (0.1 equiv). The solution of this preformed ternary complex ($[Zn^{2+}(\mathbf{2}-2H)^{2-}$(bipy)]) was then used for the cyclopropanation of cinnamyl alcohol. The product was obtained with a slightly lower enantiomeric excess (76% *ee*). Taken together, these experiments reveal that $[Zn^{2+}(\mathbf{2}-2H)^{2-}]$ retains its catalytic activity upon complexation with bipy, and that bipy is a weakly competitive ligand for the catalyst in place of the substrate and reagents in the cyclopropanation.

The most compelling evidence concerning the nature of the zinc–sulfonamide species is provided by the solid-state structure (Figure 2).[14] Single crystals of $[Zn^{2+}(\mathbf{2}-2H)^{2-}$(bipy)] suitable for X-ray diffraction analysis

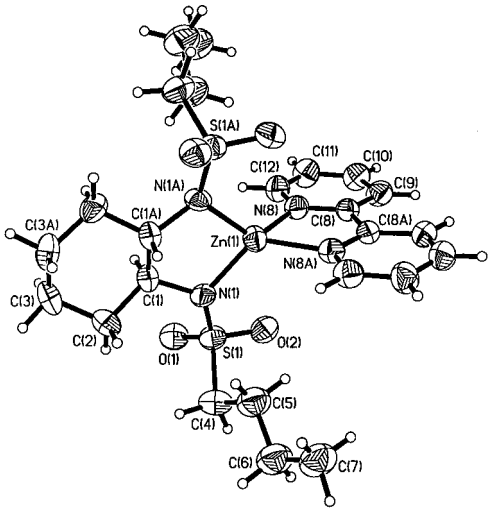


Figure 2. SHELXTL representation of the crystal structure of $[Zn^{2+}(\mathbf{2}-2H)^{2-}$(bipy)] (35% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 1.942(8), Zn(1) –N(8) 2.047(8), S(1) –N(1) 1.569(7), S(1) –O(1) 1.461(8), S(1) –O(2) 1.446(8); N(1)-Zn(1)-N(1A) 85.8(4), N(8)-Zn(1)-N(8A) 80.0(5), N(1)-Zn(1)-N(8) 124.8(3), N(1)-Zn(1)-N(8A) 123.4(3), Zn(1)-N(1)-S(1) 119.8(4); torsional angles [°]: C(4)-S(1)-N(1)-Zn(1) 119.0(10), S(1)-C(4)-C(5)-C(6) –161(2).

could be obtained by treatment of racemic **2** in $CHCl_3$ with diethylzinc (1.0 equiv) and then bipy (1.0 equiv) at room temperature followed by cooling to -20 to $-25\,^\circ$C.[15] The compound crystallized as a tris(chloroform) solvate.

The crystal structure confirmed that the zinc atom is bonded to both sulfonamide nitrogen atoms. The Zn–N bond lengths are both 1.942(8) Å, as the molecule resides on a twofold symmetry axis. The distances between zinc and the bipy nitrogen atoms are 2.047(8) Å; the four nitrogen atoms around zinc form a highly distorted tetrahedron. The sulfonamide N-Zn-N angle is contracted from the ideal tetrahedral angle of 109.5° to 85.8(4)°, whereas the N-Zn-N angle for the

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bipy ligands is 80.0(5)° owing to the long Zn – N bonds in each of the two five-membered rings. Another noteworthy feature is the pyramidality of the sulfonamide nitrogen atoms (sum of angles at N 352.3°). This places the sulfonyl groups in pseudo-equatorial orientations and clearly results from the minimization of nonbonded interactions with the cyclohexane backbone. The differential disposition of the sulfonamide groups plays a critical role in our model for asymmetric induction.[12c]

The chelation of zinc by the Lewis basic bipy nitrogen atoms suggests that the active catalyst may function in solution as a divalent Lewis acid. With our transition state model[12c] for the enantioselective cyclopropanation, we propose that the coordination sites at the zinc atom of $[Zn^{2+}(\mathbf{2}-2H)^{2-}]$ are occupied by the oxygen atom of the alkoxide and the zinc-bound iodine atom of the reagent, iodomethylzinc iodide. The crystal structure of $[Zn^{2+}(\mathbf{2}-2H)^{2-}(bipy)]$ and the data described herein provide additional support for this dual mode of action of a zinc-containing Lewis acid. The simultaneous coordination of two reactive species, namely the substrate ethylzinc alkoxide and the reagent iodomethylzinc iodide, by the zinc atom in $[Zn^{2+}(\mathbf{2}-2H)^{2-}(bipy)]$ implies that it acts as a focal point, or organizational center, and at the same time enhances the reactivity of the reagent by virtue of the electron-deficient and geometrically distorted zinc atom.

The structure of the active species in any catalytic process is difficult to guarantee. This is particularly true for a heterogeneous reaction of this complexity with many components, and $[Zn^{2+}(\mathbf{2}-2H)^{2-}]$ *may* represent a precatalyst. Nevertheless, taken together with the results from previous studies, we can now formulate a more coherent picture for the nature of the substrate[12c] as well as the structures of the reagent[12d] and the catalyst in these enantioselective cyclopropanations.

Experimental Section

2: To a solution of (*R,R*)-1,2-cyclohexanediamine (1.097 g, 9.6 mmol) and triethylamine (2.92 g, 28.9 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added *n*-butanesulfonyl chloride (3.92 g, 25.0 mmol). The reaction mixture was warmed to room temperature and stirred for 12 h. The mixture was then cooled to 0 °C, and aqueous H_2SO_4 (3.0 N, 30 mL) was added. Extraction of the aqueous layer with CH_2Cl_2 (3 × 20 mL), drying of the combined extracts ($MgSO_4$), and in vacuo concentration followed by column chromatography (silica gel, CH_2Cl_2/CH_3OH 19/1) and crystallization from hexane/CH_2Cl_2 provided 2.98 g (8.4 mmol, 87 %) of **2** as a white crystalline material. M.p. 137.0 – 138.0 °C; ^{1}H NMR (500 MHz): $\delta = 4.78$ (d, $J = 6.8$, 2H, NH), 3.06 (m, 6H, HC(1), $H_2C(4)$), 2.15 (d, $J = 12.4$, 2H, $H_{eq}C(2)$), 1.79 (m, 6H, $H_{ax}C(2)$, $H_2C(5)$), 1.46 (m, 4H, $H_2(6)$), 1.32 (m, 4H, $H_2C(3)$), 0.95 (t, $J = 7.3$, 6H, $H_3C(7)$); ^{13}C NMR (125 MHz): $\delta = 57.42$ (C1), 53.84 (C4), 34.58 (C2), 25.60 (C5), 24.63 (C3), 21.54 (C6), 13.59 (C7); MS (EI): *m/z* (%): 354 (M^+, <1), 96 (100); IR: $\tilde{\nu} = 3279$ (s), 2957 (s), 2943 (s), 2922 (s), 1451 cm^{-1} (s); TLC R_f 0.30 (CH_2Cl_2/CH_3OH, 49/1); elemental analysis calcd for $C_{14}H_{30}N_2O_4S_2$ (354.53): C 47.43, H 8.53, N 7.90, S 18.09; found: C 47.69, H 8.49, N 7.97, S 18.04.

$[Zn^{2+}(\mathbf{2}-2H)^{2-}]$: To a solution of **2** (753 mg, 2.12 mmol) in $CHCl_3$ (20 mL) at 0 °C was added diethylzinc (218 mL, 1.00 equiv), and the solution allowed to warm to room temperature. After about 10 min the precipitate became somewhat viscous, and a white, powdery precipitate formed. The contents of the flask were cooled in a liquid N_2 bath, and a vacuum (≈ 0.1 mm) was applied overnight. As the liquid N_2 was allowed to evaporate, the solvent was distilled into a liquid N_2 trap to leave an off-white powdery solid. This material was sealed under vacuum and transferred to a dry box. Samples were weighed and sealed in tin capsules for C,H,N elemental analysis and in aluminum capsules for S and Zn elemental analysis: calcd for $C_{14}H_{28}N_2O_4S_2Zn_1$ (417.89): C 40.24, H 6.75, N 6.70, S 15.34, Zn 15.65; found: C 40.39, H 6.91, N 6.66, S 14.88, Zn 15.83.

$[Zn^{2+}(\mathbf{2}-2H)^{2-}(bipy)]$: To a solution of **2** (355 mg, 1.00 mmol) in $CHCl_3$ (8.0 mL) in a 35-mL two-neck round-bottom flask fitted with a rubber septum and a ground glass gas inlet adapter but *no stirbar* was added diethylzinc (104 mL, 1.02 equiv) at room temperature. This was done while gently swirling the flask to mix the contents. After about 10 min the solution became very viscous. A solution of 2,2′-bipyridyl (156 mg, 1.00 equiv) in $CHCl_3$ (2.0 mL) was added, and the flask swirled to mix the contents. The solution was no longer viscous upon complete addition of the 2,2′-bipyridyl solution. After cooling at −20 to −25 °C in a freezer, in the absence of light, a large amount of colorless, long, thick needlelike crystals had formed. The crystals could be redissolved at 0 °C and reformed upon subsequent cooling to −20 to −25 °C for several hours. A single crystal was removed and quickly mounted in a stream of N_2 at −70 °C.

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[15] Crystal structure analysis of $[Zn^{2+}(\mathbf{2}-2H)^{2-}(bipy)]$: A single crystal grew from a solution in $CHCl_3$ at −25 °C. $C_{30}H_{42}Cl_{18}N_4O_4S_2Zn$, $M_r = 1290.27$, crystal size 0.3 × 0.3 × 1.2 mm, $a = 20.8189(6)$, $b = 16.6984(5)$, $c = 15.6761(3)$ Å, $\beta = 100.2910(10)°$, $V = 5362.0(2)$ Å^3, $\rho_{calcd} = 1.598$ g cm^{-3}, $\mu = 1.470$ mm^{-1}, empirical absorption correction, $Z = 4$, monoclinic, space group *C*2/c, Siemens three-circle platform diffractomer with Mo irradiation ($Mo_{K\alpha} = 0.71073$ Å) and a CCD area detector, $T = 198$ K; of 9873 reflections measured($\pm h$, $\pm k$, $\pm l$), 3493 were independent and 2458 observed with $I > 2\sigma(I)$; $R = 0.101$ $wR = 0.271$ (against $|F^2|$), residual electron density 1.57 e Å^{-3}; programs used: SHELXS-86, SHELXL-93. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100967. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).