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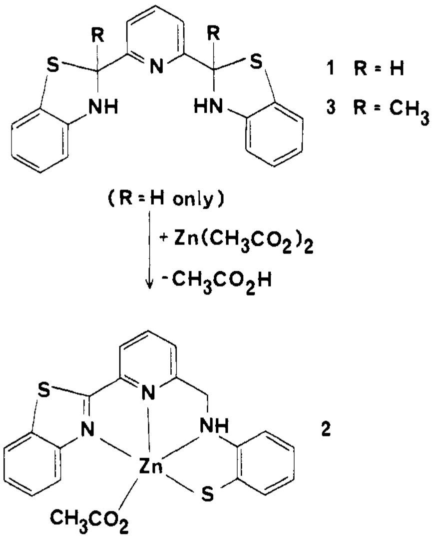
Communications to the Editor

Ligand Rearrangement Reactions. An Unusual Hydrogen Transfer Reaction Promoted by Zinc(II) Salts

Sir:

We wish to report an unusual ligand rearrangement which is promoted by divalent zinc salts and involves a net "internal hydrogen transfer" between two widely separated functional groups. This reaction is observed when a mixture of *meso*- and *rac*-2,6-bis(2-benzothiazolinyl)pyridine (**1**) is treated with zinc(II) acetate in 9:1 acetone/dimethylformamide under a dinitrogen atmosphere. The major product of this reaction (>70% yield) is [2-(2-benzothiazolyl)-6-[2-(2-thiolophenyl)-2-azaethyl]pyridine]acetatozinc(II) (**2**), in which one of the thiazoline rings has opened, and the resulting "N_3S" ligand and a monodentate acetate group define an irregular five-coordinate geometry about the zinc(II) ion (Figure 1).



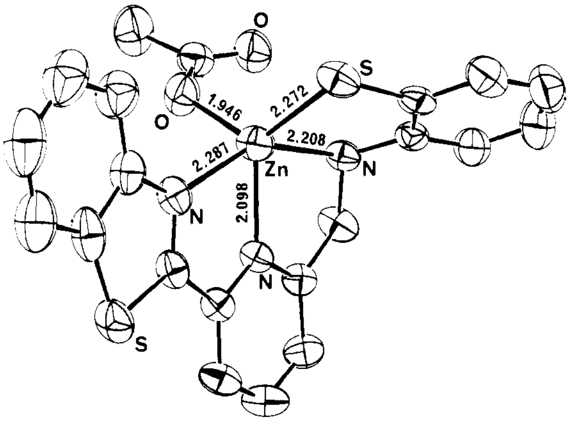


Figure 1. The structure of **2**, [2-(2-benzothiazolyl)-6-[2-thiolophenyl)-2-azaethyl]pyridine]acetatozinc(II) with selected bond lengths (Å) (mean esd, 0.006 Å).

The x-ray structure determination of **2** was accomplished using 3145 independent reflections with $I/\sigma(I) \geq 3$ and $3 < \theta < 27°$ obtained on a Philips PW1100 automatic diffractometer with graphite monochromatized Mo Kα radiation (λ 0.71069 Å).

The compound separated from the reaction mixture as orange prisms, $Zn(C_{19}H_{14}N_3S_2)\cdot CH_3CO_2$; mol wt 472.88; monoclinic; space group $P2_1/c$; $a = 12.266$ (4), $b = 9.457$ (2), $c = 19.783$ (5) Å; $\beta = 118.48$ (1)°; $U = 2017$ Å^3; $D_m = 1.54$, $D_c = 1.56$ g cm^{-3}; $Z = 4$. Full-matrix least-squares refinement[1] of the atomic parameters (all nonhydrogen atoms anisotropic) gave $R_1 = 0.042$, $R_2 = 0.053$.

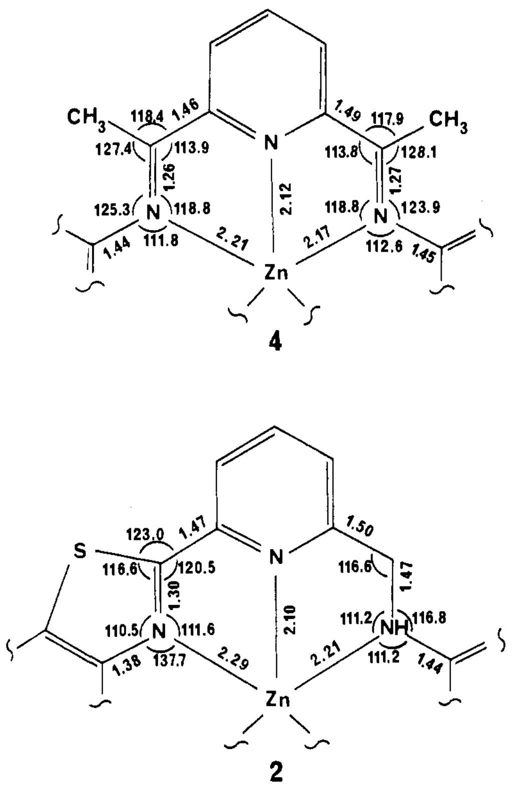
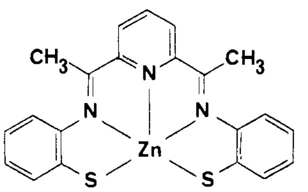


Figure 2. Bond lengths (Å) and angles (°) in the pyridino chelate rings of **4** and **2** (esd for lengths, <0.01 Å; for angles, <0.9°).

The formation of **2** was unexpected, since under identical reaction conditions the dimethyl derivative (**3**) of the 2,6-bis(2-benzothiazolinyl)pyridine gives[2] the complex **4** which has been shown[3] to have an unusual "helical" five-coordinate structure. It has been proposed that this geometry results, at least in part, from the unfavorable steric interaction between the methyl substituent on the imine group and the anil ortho-hydrogen atom. We have studied reactions of **1** in order to investigate the importance of this interaction in determining the course of metal-ion assisted syntheses of related macrocyclic ligands.[4]



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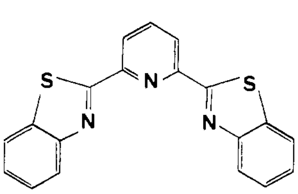
The most noteworthy feature of the formation of the product **1** is the change in hydrogenation levels of the two limbs of the ligand which accompanies the reaction (see bond lengths and angles in Figure 2). In addition to the ring opening of one of the thiazolinyl rings to give an imino thiolate chelate, a net "internal hydrogen transfer" reaction is required to account for the dehydrogenation of the other benzothiazolinyl ring and the hydrogenation of the imino linkage. Thus, the formation of **2** provides a rare example of a dehydrogenation/hydrogenation reaction which is promoted by a divalent metal ion which does not show facile oxidation state changes, and in this respect provides an analogy to the zinc-containing enzyme liver dehydrogenase. Also of interest is the formal resemblance of the N,S heterocycle to that in thiamine, which is a requisite cofactor for many enzymic reactions.

The reaction appears to be reversible since attempts to displace the ligands from the complex **2** by treating with solutions of cyanide or thiocyanate salts result in regeneration of the thiazolinyl ring, as demonstrated by the isolation of 2,6-bis(2-benzothiazolyl)pyridine (55%) (**5**)[5] after extraction of organic materials into chloroform, followed by slow crystallization in air. Formation of **2** in relatively high yields may therefore be a result of a combination of (a) its low solubility and (b) the ability of zinc(II) to act as a "thermodynamic template ion".[6] Analogous results were obtained when zinc(II) nitrate was used instead of the acetate. Mechanistic studies of this and related reactions are planned.



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A New and Highly Effective Aldol Synthesis

Sir:

Reported here is a new method for the aldol synthesis which is regiospecific, simple, and efficient. It is expected that the process will find widespread use and that in many instances it will be found superior to currently important procedures.[1] The new process may be represented by Scheme I.

In principle, organoaluminum compounds have a vast potential as an agent of aldol reaction, although this concept has not been generally accepted for synthesis owing to the lack of an effective procedure for converting a carbonyl compound into a reactive aluminum enolate.[2] The critical part of the new process (Scheme I) consists of coupled attack on the α-halo ketone by dialkylaluminum chloride and zinc which generates

Scheme I