

the same conditions as the reaction of **1**^[2], **2** resisted hydrogenation and was recovered in 81% yield, whereas **6** furnished 5-amino-1-isoquinolinecarbonitrile **7** in 72% yield, but no amide.

These results provided additional evidence in support of the proposed mechanism. Finally, we note that the orientation of nitration of 7-methoxy-6-methylisoquinoline derivatives is determined unambiguously without correlation methods or spectroscopic analysis^[5].

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[1] G. Procter, D. Britton, J. D. Dunitz, *Helv. Chim. Acta* 64 (1981) 471, and references cited therein.

[2] **1** (259 mg, 1.06 mmol) was hydrogenated in 10 mL anhydrous DMF with 201 mg 10% Pd/C (3 h). The catalyst was filtered off and removal of the solvent gave 225 mg crude material, chromatography of which on 7 g silica gel (Kieselgel 60) afforded 97 mg (43.0%) **2**, m. p. = 137.5–138.5 °C (*n*-hexane). Elution with *n*-hexane/ethyl acetate (1:1), and *n*-hexane/ethyl acetate (1:1/1:2) gave 84 mg of the eluate, which after preparative thin layer chromatography on silica gel (CH₂Cl₂/acetone 1:1) yielded 31 mg (12.7%) **3**, m. p. = 104.5–106.0 °C (benzene) [**3**], 13 mg (5.7%) **4**, m. p. 262.5–264.0 °C (acetone) [**3**] and 34 mg (17.2%) **5**, m. p. = 78.0–79.0 °C (*n*-hexane).

[3] **3**: IR (KBr): 1560, 1630, 1658, 3340 cm⁻¹; UV (EtOH): λ_{max} = 212 nm (log ε = 4.59), 252 (4.42), 323 (sh, 3.50), 365 (3.58); ¹H-NMR (CDCl₃): δ = 2.37 (s, 3H), 3.75 (s, 3H), 5.60 (br s, 2H, D₂O exchangeable), 6.56 (br s, 1H, D₂O exchangeable), 6.95 (s, 1H), 7.43 (d, *J* = 8 Hz, 1H), 7.52 (br s, 1H, D₂O exchangeable), 8.13 (d, *J* = 8 Hz, 1H); MS: *m/z* 231 (*M*⁺, 63%), 216 (54), 199 (100), 171 (57).—**4**: IR (KBr): 1490, 1590, 1635, 1690, 3190 cm⁻¹; UV (EtOH): λ_{max} = 217 nm (log ε = 4.39), 259 (4.35), 345 (3.17), 392 (3.40); ¹H-NMR (D₂S)pyridine): δ = 2.37 (s, 3H), 4.27 (s, 3H), 7.25 (s, 1H), 7.64 (d, *J* = 8 Hz, 1H), 8.92 (d, *J* = 8 Hz, 1H), 11.84 (s, 1H, D₂O exchangeable); MS: *m/z* 214 (*M*⁺, 100%), 199 (63), 171 (56), 116 (15).

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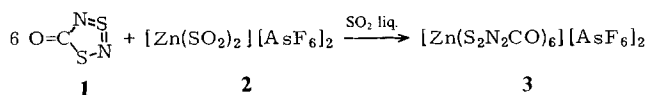
[5] S. F. Dyke in S. Coffey: *Rodd's Chemistry of Carbon Compounds*, 2nd ed., Elsevier, Amsterdam 1976, Vol. IV, Part F, Chapt. 27.

Synthesis and Structure of [Zn(S₂N₂CO)₆][AsF₆]₂—Sulfur-Nitrogen Rings as Ligands in Coordination Compounds**

By Herbert W. Roesky*, Manfred Thomas, Mathias Noltemeyer, and George M. Sheldrick

Dedicated to Professor Rudolf Hoppe on the occasion of his 60th birthday

5-Oxo-1,3λ⁴,2,4-dithiadiazole **1** can be prepared by reaction of [(CH₃)₂SnN₂S₂]₂ with carbonyl difluoride^[1]. In order to clarify whether the coordination of the ligand to a metal atom takes place *via* oxygen, sulfur or nitrogen, we have investigated the reaction of **1** with the zinc complex **2** in liquid SO₂.



After removal of SO₂, **3** precipitates as a colorless solid. **3** (m. p. 150 °C) is recrystallized from liquid SO₂; it is insoluble in CH₂Cl₂. Owing to their modest donor properties, the ligands **1** in **3** are very readily replaced by water mole-

cules. In the IR spectrum of **3** the C=O stretching vibration is observed at 1560 cm⁻¹, *i. e.* it is shifted by 167 cm⁻¹ to lower wave numbers compared to that of **1**. Thus, **1** should be coordinated to zinc *via* oxygen.

The X-ray structure determination shows that **3** crystallizes in the space group P $\bar{3}$ with *a* = *b* = 1190.1(1), *c* = 665.1(1) pm and *Z* = 1, ρ_{calc} = 2.37 Mg m⁻³. The structure was solved by direct methods and refined to *R* = 0.046 and *R*_w = 0.049 for 1498 independent reflections with *F*₀ > 3σ(*F*₀) and MoK α -radiation.

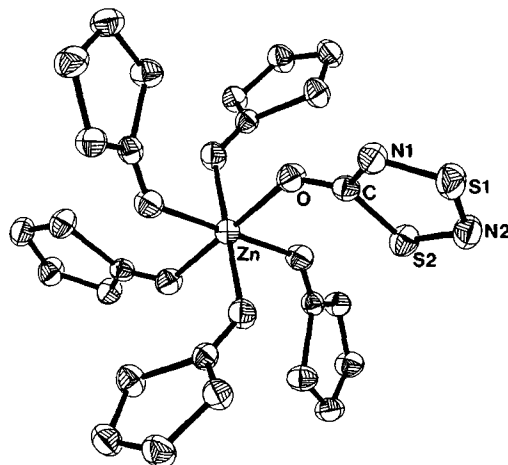


Fig. 1. Structure of [Zn(S₂N₂CO)₆]²⁺, atom numbering and interatomic distances [pm], standard deviations in brackets: C—N(1) 134.7(3), N(1)—S(1) 157.6(3), S(1)—N(2) 157.0(3), N(2)—S(2) 161.7(2), S(2)—C 178.9(3), O—C 124.0(3).

In the Zn(S₂N₂CO)₆²⁺ cation (Fig. 1) Zn is octahedrally coordinated: The maximum distortion from 90° is 1.4°. Zn lies on the special position with $\bar{3}$ symmetry and As on a threefold axis. The ligand **1**^[2] is planar within experimental error, and possesses no crystallographic symmetry. The Zn—O—C angle is 134.2°. The C—O bond length in **3** (124.0(3) pm) is somewhat longer than in the free ligand (122.2(7) pm). The remaining bond lengths within the S₂N₂C ring show no significant change; the average S—N bond length in the uncoordinated ligand **1** is 159.5 and in **3** 158.8 pm.

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CAS Registry numbers:
2, 83416-63-1; 3, 83416-61-9.

[1] H. W. Roesky, H. Wierzer, *Angew. Chem.* 87 (1975) 254; *Angew. Chem. Int. Ed. Engl.* 14 (1975) 258.

[2] H. W. Roesky, E. Wehner, E. J. Zehnder, H. J. Deiseroth, A. Simon, *Chem. Ber.* 111 (1978) 1670.

Tl(O^{*t*}Bu)₃Sn: A Small Pentatomic Cage Molecule**

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It is known that heavy main-group elements in low oxidation states can occur as essential constituents of cage

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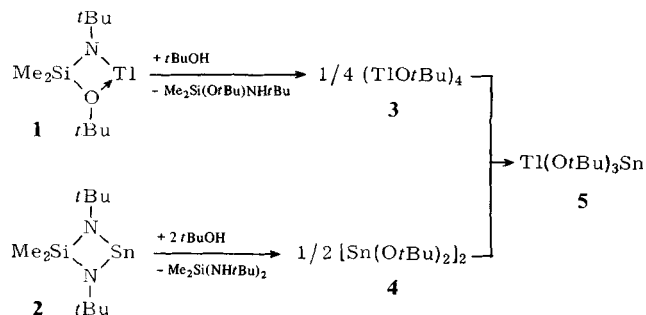
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molecules. Hence, *e.g.* $\text{TlOCH}_3^{[1]}$ and $t\text{BuN}=\text{Sn}^{[2]}$ form tetramers, which consist of cubane-like Tl_4O_4 and Sn_4N_4 cages, respectively. In these compounds the main-group elements achieve a noble gas configuration through coordinative bonds.

We have now succeeded, for the first time, using Tl^{I} and Sn^{II} , in incorporating two low-valent elements from different main groups into a cage: for this purpose we made use of methods which we previously developed for the synthesis of Sn^{II} polycycles^[2]. The pentatomic cage system **5** is obtained in high yield from the Tl^{I} and Sn^{II} molecular compounds **1**^[3a] and **2**^[3b] by allowing these to react with *tert*-butyl alcohol and subsequent reaction of the isolable intermediates of tetrameric **3**^[4] and dimeric **4**.



5 is sublimable at $40^\circ\text{C}/0.001$ torr, soluble in benzene, and displays only one signal ($\delta=1.32$) in the $^1\text{H-NMR}$ spectrum, which indicates a highly symmetric molecule. The C_3 symmetry of the molecule is confirmed by X-ray structural analysis (Fig. 1). Tl and Sn are held together by three *tert*-butoxy ligands, which results in a trigonal bipyramid: three oxygen atoms form the triangle, whereas the metal atoms are situated on the vertices.

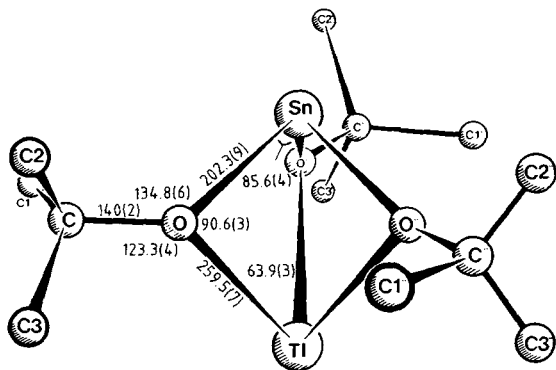
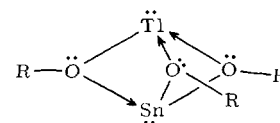


Fig. 1. Perspective representation of **5** with bond lengths [pm] and angles $^\circ$. Crystal data: hexagonal, space group $\text{P6}_3/\text{m}$; $a=994.4(5)$, $c=1107(1)$ pm; $Z=2$; $\rho_{\text{exp}}=1.90$ g \cdot cm $^{-3}$. 352 independent reflections, $R=0.053$. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, by quoting the following number CSD 50257, the name of the author, and the journal citation.

Due to the "encircling" the tin and thallium atoms come as close as $330.6(3)$ pm to each other. The relatively short $\text{SnO}^{[2]}$ and TlO distances^[5] allow it to be presumed that an intramolecular ion pair, such as $\text{Tl}^{\oplus}[(\text{OtBu})_3\text{Sn}]^{\ominus}$, is involved in **5**. This description, however, only corresponds to a mesomeric structure. The good solubility in benzene, ease of sublimation, and, above all, the crystal structure clearly indicate the nonpolar character of the molecule. In

the crystal the molecules are arranged in a layer sequence AB, AB, \dots , in which a statistical defect along the hexagonal axis is observed (crystallographic point symmetry of **5**: C_{3h} ($3/\text{m}$)). The bonding behavior in the cage molecule **5** can be described thus:



According to the structural determination, the two-electron donor bonds are indistinguishable from the two electron single bonds.

Procedure

tert-Butyl alcohol (0.59 g, 0.008 mol resp. 1.2 g, 0.016 mol), is added dropwise to a solution of **1**^[3a] (3.26 g, 0.008 mol) and **2**^[3b] (2.58 g, 0.008 mol), respectively, in diethyl ether (20 mL) at -10°C . Both solutions are stirred for 30 min and then combined. The reaction mixture is separated *in vacuo* whereby 3.9 g (90%) of colorless crystals of **5** sublime, which melt at 43°C .

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1, 83437-07-4; **2**, 54724-62-8; **3**, 22520-89-4; **4**, 3275-19-2; **5**, 83437-08-5.

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New Dihydropyrans: Lewis Acid Catalyzed Cycloadditions of α,β -Unsaturated Acyl Cyanides to Simple, Unactivated Olefins and Dienes: A Readily Accessible Route to Derivatives of Rose Oxide**

By Zeinhor M. Ismail and H. M. R. Hoffmann*

Cycloadditions of α,β -unsaturated carbonyl compounds to electron-rich olefins^[1] are classified as Diels-Alder reactions with inverse electron-demand and furnish 3,4-dihydropyrans: Typically, enol ethers react with α,β -unsaturated aldehydes on heating in an autoclave at $160\text{--}180^\circ\text{C}$ (see *e.g.* formation of **3a** in Table 1). Previously, intermolecular cycloadditions of simple alkenes to α,β -unsaturated carbonyl compounds were unknown^[2].

We have recently prepared a variety of α,β -unsaturated acyl cyanides^[3] and now report that they can be activated by AlCl_3 to react with simple olefins at room temperature, giving novel dihydropyrans, *e.g.* **3b–3e**, in good yield. Even isobutene, **1e**, reacts with **2a** to give **3e** having two quaternary centers.

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