

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

## Stereo- and Enantioselective Reactions of Organosulfur Compounds Mediated by Transition Metal Complexes

Wolfdieter A. Schenk<sup>a</sup>; Jürgen Bezler<sup>a</sup>; Nicolai Burzlaff<sup>a</sup>; Eberhard Dombrowski<sup>a</sup>; Jürgen Frisch<sup>a</sup>; Nikolai Kuhnert<sup>a</sup>; Irene Reuther<sup>a</sup>

<sup>a</sup> Institut für Anorganische Chemie, Universität Würzburg, Würzburg, Germany

**To cite this Article** Schenk, Wolfdieter A. , Bezler, Jürgen , Burzlaff, Nicolai , Dombrowski, Eberhard , Frisch, Jürgen , Kuhnert, Nikolai and Reuther, Irene(1994) 'Stereo- and Enantioselective Reactions of Organosulfur Compounds Mediated by Transition Metal Complexes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 95: 1, 367 – 370

**To link to this Article:** DOI: 10.1080/10426509408034239

**URL:** <http://dx.doi.org/10.1080/10426509408034239>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

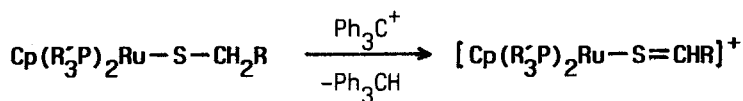
## STEREO- AND ENANTIOSELECTIVE REACTIONS OF ORGANOSULFUR COMPOUNDS MEDIATED BY TRANSITION METAL COMPLEXES

WOLFDIETER A. SCHENK\*, JÜRGEN BEZLER, NICOLAI BURZLAFF, EBERHARD DOMBROWSKI, JÜRGEN FRISCH, NIKOLAI KUHNERT, and IRENE REUTHER  
 Institut für Anorganische Chemie, Universität Würzburg,  
 Am Hubland, D-97074 Würzburg (Germany)

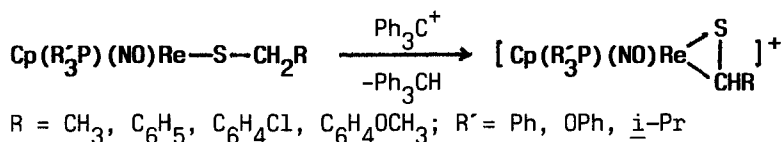
**Abstract** A number of otherwise unstable organic sulfur compounds such as thioaldehydes, sulfines, and sulfenes, can be produced and stabilized in the coordination sphere of pseudotetrahedral half-sandwich type complexes of ruthenium and rhenium. These complexes can then be used for different types of stereoselective addition reactions. Similarly  $[\text{CpRu}(\text{S,S-chiraphos})]^+$  can be used as a chiral auxiliary in the enantioselective oxidation of thioethers. Facile demetalation reactions are also available to liberate the organic product from the complex.

### THIOALDEHYDES

Recently we have found a new synthetic access to complexes of aromatic thioaldehydes.<sup>1</sup>

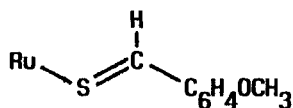


With sterically undemanding phosphine ligands ( $\text{Me}_3\text{P}$ ,  $\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2$ ) these complexes exist as rapidly equilibrating mixtures of  $\eta^1$  and  $\eta^2$  isomers. The reaction can be extended to  $\eta^2$ -thioaldehyde complexes of rhenium which are obtained as diastereomerically pure pairs of (RR,SS) enantiomers.<sup>2</sup>

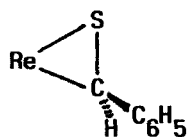


X-Ray structure determinations show that in the  $\eta^1$  form the C-S distance is that of a double bond ( $163.2 \text{ pm}^1$ ) while in the  $\eta^2$  form this

bond is lengthened to 170 pm.<sup>2</sup>



Ru-S 231.4 pm  
S-C 163.2 pm

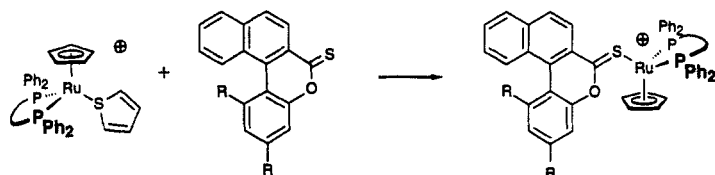


Re-S 237.6 pm  
S-C 170 pm  
Re-C 220.7 pm

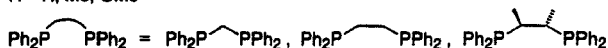
The thioaldehyde complexes undergo Diels-Alder additions with cyclopentadiene as well as open-chain dienes. The additions are only moderately diastereoselective (20 - 40 %de) but, in the case of cyclopentadiene, highly exo-selective.

### THIOLACTONES

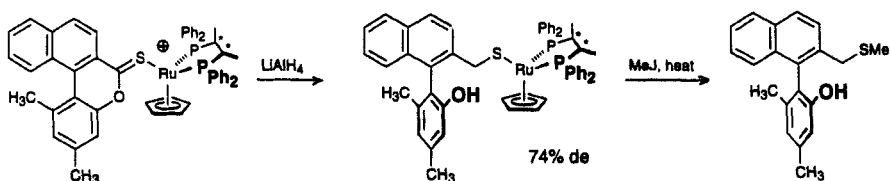
Biaryl-thiolactone complexes are obtained via a simple ligand exchange.<sup>3</sup>



R = H, Me, OMe

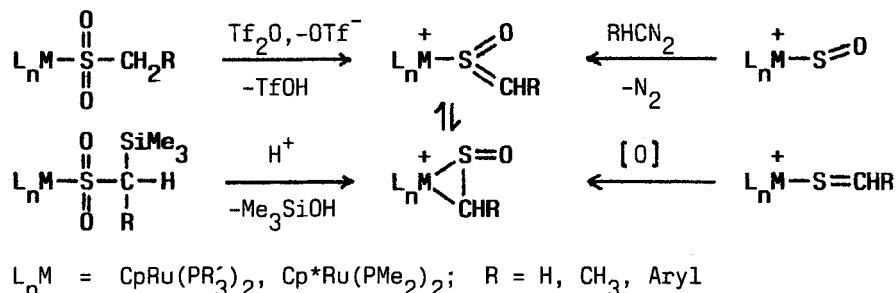


The complex  $[\text{CpRu}(\text{S,S-chiraphos})]^+$  is well-suited as a chiral auxiliary to effect an enantioselective ring-opening of the thiolactone bridge, as shown in the following equation.

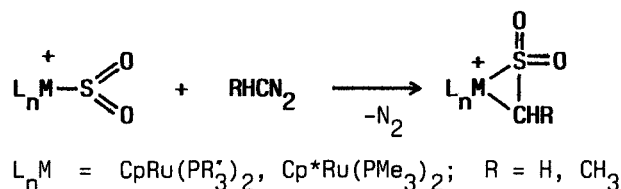


SULFINES

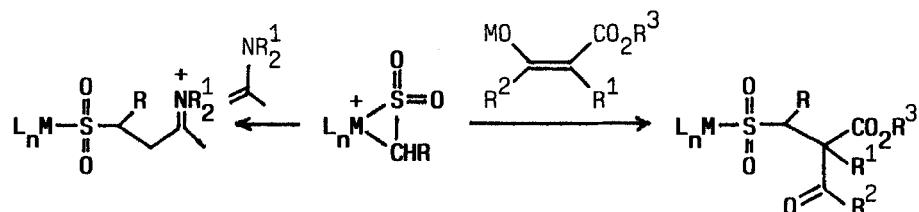
For the synthesis of sulfine complexes a number of methods are now available, including elimination reactions of sulfinato complexes, methylene transfer to SO complexes, and oxidation of thioaldehyde complexes.

SULFENES

Similar sulfene complexes have recently been obtained by methylene addition to  $\text{SO}_2$  complexes.<sup>4</sup>



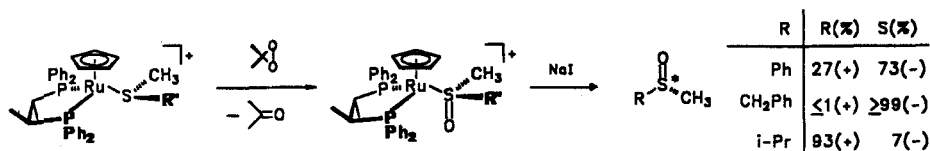
The high electrophilicity of these compounds can be exploited for C-C coupling reactions with, e.g., enamines and metalated  $\beta$ -ketoesters.



For  $\text{R} = \text{CH}_3$  these additions occur with high diastereoselectivities. Decomplexation routes to give esters of either the corresponding sulfonic or sulfinic acids have also been developed.

## SULFOXIDES

Transition-metal coordinated thioethers can in favorable circumstances be oxidized to sulfoxide complexes. Again,  $\text{CpRu}(\text{S,S-chiraphos})$  is a suitable chiral auxiliary which renders this reaction enantioselective.<sup>5</sup>



Decomplexation of the sulfoxide is achieved by heating the complex with sodium iodide in acetone.

## ACKNOWLEDGMENT

Some of this work was carried out in collaboration with W. Adam (Würzburg) and G. Bringmann (Würzburg). We thank the Deutsche Forschungsgemeinschaft (SFB 347) for financial support.

## REFERENCES

1. W. A. Schenk, T. Stur, and E. Dombrowski, J. Organomet. Chem. 472 (1994) 257.
2. W. A. Schenk, N. Burzlaff, and H. Burzlaff, Z. Naturforsch., Teil B, in print.
3. G. Bringmann, B. Schöner, O. Schupp, W. A. Schenk, I. Reuther, K. Peters, E. M. Peters, and H. G. von Schnering, J. Organomet. Chem. 472 (1994) 275.
4. W. A. Schenk, P. Urban, and E. Dombrowski, Chem. Ber. 126 (1993) 679.
5. W. A. Schenk, J. Frisch, W. Adam, and F. Prechtel, Angew. Chem., in print.