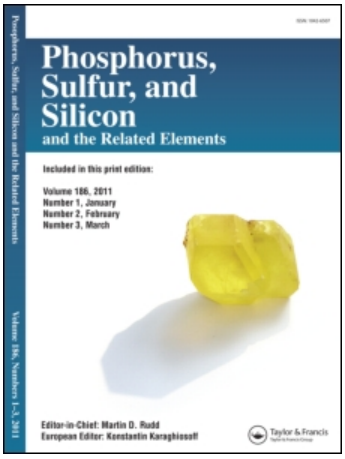
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

New Titanocene Complexes [$C_{p2}Ti(\mu\text{-}S_2)_2NR$] (with R = Me and nOct) as Transfer Reagents for the Synthesis of the Heterocycles S_5NR and S_6NR

Oliver Schumann; Ralf Steudel

To cite this Article Schumann, Oliver and Steudel, Ralf(1997) 'New Titanocene Complexes [$C_{p2}Ti(\mu\text{-}S_2)_2NR$] (with R = Me and nOct) as Transfer Reagents for the Synthesis of the Heterocycles S_5NR and S_6NR', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 529 — 532
To link to this Article: DOI: 10.1080/10426509708545676
URL: http://dx.doi.org/10.1080/10426509708545676

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.

Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 529–532
Reprints available directly from the publisher
Photocopying permitted by license only

© 1997 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia.

NEW TITANOCENE COMPLEXES $[Cp_2Ti(\mu\text{-}S_2)_2NR]$ (WITH R = Me AND ^{n}Oct) AS TRANSFER REAGENTS FOR THE SYNTHESIS OF THE HETEROCYCLES S_5NR AND S_6NR [1]

OLIVER SCHUMANN and RALF STEUDEL*
Institut für Anorganische und Analytische Chemie,
Technische Universität Berlin, D-10623 Berlin, Germany

Downloaded At: 17:41 28 January 2011

The reaction of 1,4-$S_4(NR)_2$ with $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ yields $[Cp_2Ti(\mu\text{-}S_2)_2NR]$ which on treatment with SCl_2 or S_2Cl_2 provides the novel heterocycles S_5NR and S_6NR (R = Me, Oct).

Keywords: S–N heterocycles; titanocene complexes

Cyclic sulfur imides of the type S_nNH and their derivatives S_nNR form homologous series[2] but so far only rings with more than 6 sulfur atoms have been known. We here present a synthetic method which for the first time allows the preparation of the species S_5NR and S_6NR. Titanocene dicarbonyl reacts with *cyclo*-tetrasulfur-1,4-diimides at room temperature in *n*-hexane to give the novel metallacycles $[Cp_2Ti(\mu\text{-}S_2)_2NR]$ in ca. 30% yield:

$[Cp_2Ti(CO)_2] + 1,4\text{-}S_4(NR)_2 \rightarrow$

$[Cp_2Ti(\mu\text{-}S_2)_2NR] + 2\ CO$ + byproducts

1: Cp = C_5H_5, R = Me: black crystals, m.p. 134°C

2: Cp = C_5H_5, R = ^{n}Oct: dark-brown oil

3: Cp = C_5H_4Me, R = ^{n}Oct: dark-brown oil

The ^{1}H NMR spectra of **1** and **2** show that the six-membered rings are rigid at 23°C (two signals for the Cp protons) and that the connectivity is as shown above (mirror plane for the ring atoms). An X-ray structural analysis of **1** revealed a molecule similar to the well known titanocene complexes $[Cp_2TiS_5]$ and $[Cp_2Ti(\mu\text{-}S_2)_2AsMe]$[3]:

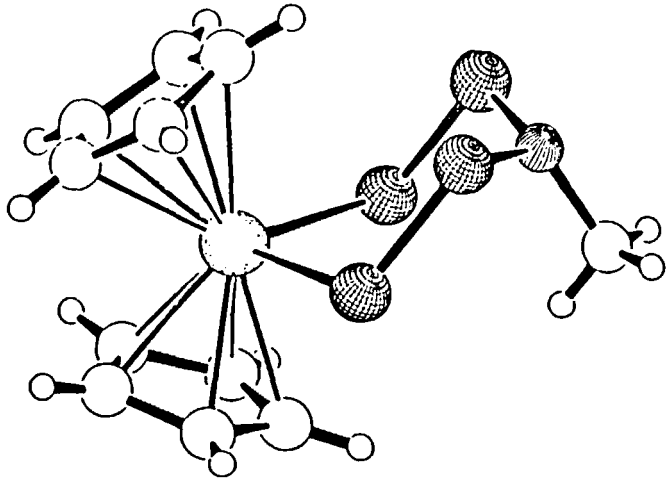


FIGURE 1 X-Ray structure of **1**

The molecules of **1** occupy general sites, and the geometrical

Downloaded At: 17:41 28 January 2011

parameters are as expected, e.g.: d_{SS} = 206pm, d_{SN} = 169 and 170 pm. The geometry at the nitrogen atom is only slightly pyramidal (sum of bond angles 347°) with the methyl group in an axial position. The values of the torsion angles of the heterocycle range from 55 to 83°.

The complexes **1-3** react rapidly and quantitatively with either SCl_2 or S_2Cl_2 at 20°C in CS_2 solution to give the novel *cyclo*-sulfurimides S_5NR resp. S_6NR besides $[Cp_2TiCl_2]$:

$$[Cp_2Ti(\mu\text{-}S_2)_2NR] + S_nCl_2 \rightarrow S_{n+4}NR + [Cp_2TiCl_2]$$

The progress of these reactions may be monitored by RP-HPLC since the retention times of the species $S_{n+4}NR$ systematically increase with increasing size of both R and of the ring as has already been observed for similar homologous series of compounds.

S_5N^nOct and S_6N^nOct have been isolated as pale-yellow oils which are stable at ambient temperature for a few hours and at –25°C for several days. The new compounds have been characterized by EI-MS (molecular ions observed) and ^1H NMR spectra. S_7N^nOct was prepared from S_7NH and octyliodide[4] for comparison. The chemical shifts of the α and β protons of the octyl groups attached to these S–N heterocycles depend on the ring size as the following data show: ($CDCl_3$; 23°C):

Downloaded At: 17:41 28 January 2011

TABLE I ^{1}H NMR data of $S_nN^nC_8H_{17}$ (n = 5, 6 and 7)

$S_5N^nC_8H_{17}$	$S_6N^nC_8H_{17}$	$S_7N^nC_8H_{17}$	
3.90 t (2)	3.20 t (2)	3.28 t (2)	α-CH_2
1.60 q (2)	1.70 q (2)	1.69 t (2)	β-CH_2
1.29 m (10)	1.30 m (10)	1.30 m (10)	-$(CH_2)_5$-
0.89 t (3)	0.89 t (3)	0.90 t (3)	-CH_3

Downloaded At: 17:41 28 January 2011

Acknowledgement

We are grateful to Prof. P. Luger and Dr. J. Buschmann of the Freie Universität Berlin for the X-ray structural analysis and to the Deutsche Forschungsgemeinschaft for support.

References:

[1] Sulfur Compounds, Part 202; for Part 201 see Y. Drozdova, R. Steudel, *Phosphorus, Sulfur, Silicon*, in print.

[2] R. Steudel, K. Bergemann, J. Buschmann, P. Luger, *Angew. Chem. Int. Ed. Engl.* **35**, 2537 (1996), and cit. lit.

[3] R. Steudel, B. Holz, J. Pickardt, *Angew. Chem. Int. Ed. Engl.* **28**, 1269 (1989).

[4] B.A. Olsen, F.P. Olsen, *Inorg. Chem.* **8**, 1739 (1969).