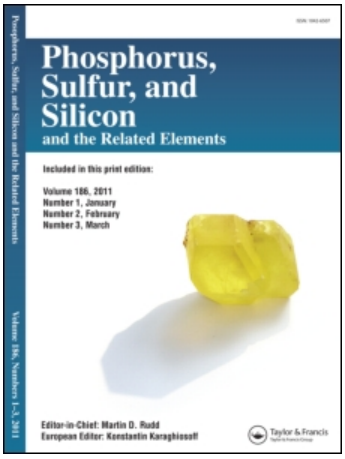

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Silicon- and Germanium-Containing Titanocene Chalcogenide Complexes as Transfer Reagents in Ring Synthesis[1]

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To cite this Article Albertsen, Jörg and Steudel, Ralf(1992) 'Silicon- and Germanium-Containing Titanocene Chalcogenide Complexes as Transfer Reagents in Ring Synthesis[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 165 — 168
To link to this Article: DOI: 10.1080/10426509208055344
URL: http://dx.doi.org/10.1080/10426509208055344

Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 165–168

SILICON- AND GERMANIUM-CONTAINING TITANOCENE CHALCOGENIDE COMPLEXES AS TRANSFER REAGENTS IN RING SYNTHESIS[1]

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ABSTRACT The silicon- and germanium-containing titanocene complexes $Cp_2TiS_2Si(C_6H_5)_2$ and $Cp_2TiS_2Ge(C_6H_5)_2$ ($Cp = \eta^5$-C_5H_5) react with S_2Cl_2 and $(CH_2SCl)_2$, respectively, to give five- and seven-membered heterocycles which have been characterized by mass and ^1H NMR spectroscopy.

INTRODUCTION

Titanocene chalcogenide complexes like Cp_2TiS_5 **1**, $Cp_2TiS_4C(CH_3)_2$ **2** and others have been used to transfer the chelate ligand under mild conditions to synthesize sulfur homocycles[2,3] and sulfur-rich heterocycles[4–7] with carbon, phosphorus, arsenic and other ring constituents, e. g. see equations (1) and (2):

$$Cp_2TiS_5 + S_2Cl_2 \longrightarrow S_7 + Cp_2TiCl_2 \quad (1)$$

$$Cp_2TiS_4C(CH_3)_2 + S_2Cl_2 \longrightarrow S_6C(CH_3)_2 + Cp_2TiCl_2 \quad (2)$$

In this work it is shown that the recently prepared titanocene complexes $Cp_2TiS_2Si(C_6H_5)_2$ **3** and $Cp_2TiS_2Ge(C_6H_5)_2$ **4**[8] can be used as transfer reagents for $S_2E(C_6H_5)_2$ groups (E = Si, Ge).

REACTIONS AND PRODUCTS

All reactions have been carried out in carbon disulfide solution under exclusion of air and moisture at temperatures below −50°C.

When **3** and **4** were treated with S_2Cl_2 in a molar ratio of 1:1 the following reactions (3) and (4) occurred as indicated by the color change from green to red.

$$Cp_2TiS_2Si(C_6H_5)_2 + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + S_4Si(C_6H_5)_2 \quad (3)$$

$$Cp_2TiS_2Ge(C_6H_5)_2 + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + S_4Ge(C_6H_5)_2 \quad (4)$$

The five-membered heterocycles $S_4Si(C_6H_5)_2$ **5** and $S_4Ge(C_6H_5)_2$ **6** have been isolated from the dried reaction mixture with n-pentane at below −20°C. Both compounds are colorless, waxy solids which are stable below −20°C in an inert atmosphere. Table 1 shows the analytical data of **5** and **6**.

Table 1. ^{1}H NMR and mass spectra of **5** and **6**

	$S_4Si(C_6H_5)_2$ **5**	$S_4Ge(C_6H_5)_2$ **6**
^{1}H NMR [ppm]: ($CDCl_3$)	7.88 – 7.65 m	7.85 – 7.65 m
	7.59 – 7.36 m	7.59 – 7.42 m
EI-MS (70 eV):	M^+ 310 (3%)	M^+ 356 (10%)
	M^+-S 278 (5%)	
	M^+-S_2 246 (10%)	M^+-S_2 292 (21%)

Using the bis(sulfenyl chloride) of ethane instead of S_2Cl_2 under the same

conditions, the germanium containing complex showed a lower reactivity than the silicon homologue. No reaction took place with the germanium complex below 0°C while the silicon compound reacts even at −50°C. As shown in equations (5) and (6) the seven-membered heterocycles $C_2H_4S_4Si(C_6H_5)_2$ **7** and $C_2H_4S_4Ge(C_6H_5)_2$ **8** were obtained.

$$Cp_2TiS_2Si(C_6H_5)_2 + (CH_2SCl)_2 \longrightarrow Cp_2TiCl_2 + C_2H_4S_4Si(C_6H_5)_2 \quad (5)$$

$$Cp_2TiS_2Ge(C_6H_5)_2 + (CH_2SCl)_2 \longrightarrow Cp_2TiCl_2 + C_2H_4S_4Ge(C_6H_5)_2 \quad (6)$$

The two methylene groups of the heterocycles **7** and **8** are equivalent on the NMR time scale as shown by the spectroscopic data in Table 2. The mass spectra exhibit the molecular ions, and $C_2H_4S_3^+$ is observed with high intensity as a characteristic fragment of sulfur-rich heterocycles containing a C_2H_4 group attached to sulfur atoms [9].

Table 2. ^{1}H NMR and mass spectra of **7** and **8**

	$C_2H_4S_4Si(C_6H_5)_2$ **7**	$C_2H_4S_4Ge(C_6H_5)_2$ **8**
^{1}H NMR [ppm]: ($CDCl_3$)	7.67 – 7.64 m	7.84 – 7.61 m
	7.52 – 7.37 m	7.59 – 7.37 m
	3.37 s	3.36 s
EI–MS (70 eV):	M^+ 338 (7%)	M^+ 384 (1%)
	M^+-S_2 274 (3%)	
	$C_2H_4S_2Si(C_6H_5)^+$ 197 (59%)	
	$C_2H_4S_3^+$ 124 (47%)	$C_2H_4S_3^+$ 124 (40%)

CONCLUSION

Our results show that SCl group containing reagents attack primarily the titanium–sulfur bond of the complexes **3** and **4**. Neither the NMR nor the mass spectra gave evidence for the formation of any organano chloro silane or germane, respectively. Thus, the $S_2E(C_6H_5)_2$ unit has been transferred to form novel sulfur–rich heterocycles.

Support by the Deutsche Forschungsgemeinschaft and Verband der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1) Sulfur Compounds, Part 154; for Part 153 see M. Papavassiliou, J. Pickardt and R. Steudel, Phosphorus Sulfur Silicon, preceding publication.
2) M. Schmidt, B. Block, H. D. Block, H. Köpf, and E. Wilhelm, Angew. Chem., 80, 660 (1968); Angew. Chem., Int. Ed. Engl., 7, 632 (1968) .
3) R. Steudel in Sulfur: Its Significance for Chemistry, for the Geo–, Bio– and Cosmosphere and Technology (A.Müller and B. Krebs, Eds.), Elsevier Science Publ., Amsterdam 1984, 3–37.
4) R. Steudel, R. Strauss, and D. Jensen, Chemikerztg. 109, 349 (1985).
5) R. Steudel and M. Kustos, Phosphorus Sulfur Silicon, in print.
6) B. Holz and R. Steudel, unpublished results; B. Holz, Dissertation, Techn. Univ. Berlin 1991.
7) R. Steudel, B. Holz and J. Pickardt, Angew. Chem. 101, 1301 (1989) ; Angew. Chem., Int. Ed. Engl., 28, 1269 (1989).
8) J. Albertsen and R. Steudel, J. Organomet. Chem., submitted.
9) R. Steudel, S. Förster and J. Albertsen, Chem. Ber., 124, 2357 (1991).