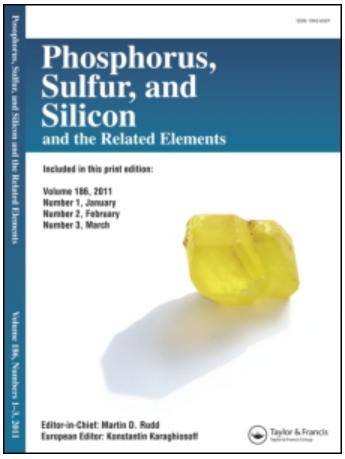

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Synthesis and Reactions of Titanacycles Containing Group 14 Elements

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SYNTHESIS AND REACTIONS OF TITANACYCLES CONTAINING GROUP 14 ELEMENTS

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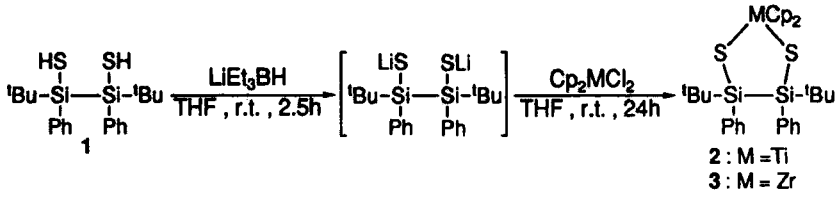
Abstract Lithium1,2-di-*tert*-butyl-1,2-diphenyldisilane-1,2-dithiolate reacted with titanocene dichloride to afford *cis*-3,4-di-*tert*-butyl-3,4-diphenyl-2,5-dithia-3,4-disila-1-bis(cyclopentadienyl)titanacyclopentane (**2**), whose structure was determined by X-ray analysis. When the titanacycle **2** or its zirconium analogue **3** is converted with electrophilic reagents (SCl_2, S_2Cl_2, $PhPCl_2$, Ph_2GeCl_2), heterocycles resulting from substitution of the titanocene moiety are obtained.

INTRODUCTION

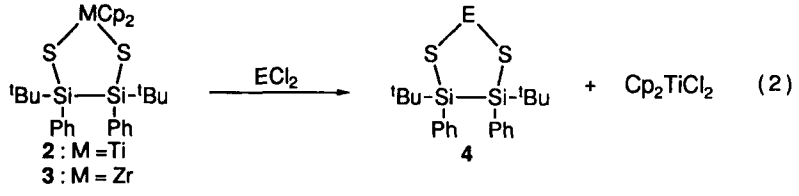
The chemistry of metallacycles with incorporated titanocene units[1] has attracted much interest, and these compounds have found widespread applications in organic synthesis.[2] Nevertheless, the utility of these promising building blocks as precursors for silicon containing heterocycles has not been fully explored.[3] Herein we wish to report the synthesis of a novel *cis*-3,4-di-*tert*-butyl-3,4-diphenyl-2,5-dithia-3,4-disila-1-bis(cyclopentadienyl)titanacyclopentane (**2**) and its zirconium analogue **3** and furthermore demonstrate the suitability of these compounds as precursors for a variety of heterocycles containing a 1,4-dithia-2,3-disila fragment.

SYNTHESIS AND REACTIONS

Cis-3,4-di-*tert*-butyl-3,4-diphenyl-2,5-dithia-3,4-disila-1-bis(cyclopentadienyl)titanacyclopentane (**2**) and its corresponding zirconacycle **3** were synthesized as outlined in Eq. 1.



Titanacycle **2** was isolated by preparative GPC (eluent : toluene) in 80% yield as green color crystals. Moisture sensitive zirconacycle **3** was purified by recrystallization of crude product under argon atmosphere.



(2)

Table 1. Reactions of Disilametallacycle **2** (**3**) with Various Electrophilic Reagents.

run		E[a)]	Solvent	Temp/°C	Time/h	Isolated Yield/%
1	**4a**	S	CS_2	-78	0.5	90 (41)
2	**4b**	SS	CS_2	-78	0.5	92 (66)
3	**4c**	PhP	Benzene	20	1	42 (49)
4	**4d**	Ph_2Ge	Toluene	110	24	55
5	**4e**	Ph_2Si	Xylene	140	72	— (—)

a) The corresponding dichlorides ECl_2 were employed as reagents.

Titanacycle **2** reacted with several electrophilic reagents under substitution of the titanocene unit to yield heterocycles in fair to good yields (Eq. 2, Table 1). While the conversions with the sulfur electrophiles easily proceeded for the transformations of **2** with $PhPCl_2$, and especially with Ph_2GeCl_2 (Table 1, entries 3,4) more drastic conditions, *i. e.* evaluated temperature and prolonged reaction time were necessary to achieve full conversion. Nevertheless, it was not possible to convert **2** with Ph_2SiCl_2; even after 72 h in refluxing xylene only unreacted **2** was re-isolated. Reactivity for electrophiles between **2** and **3** is not so much different as shown in Table 1.

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