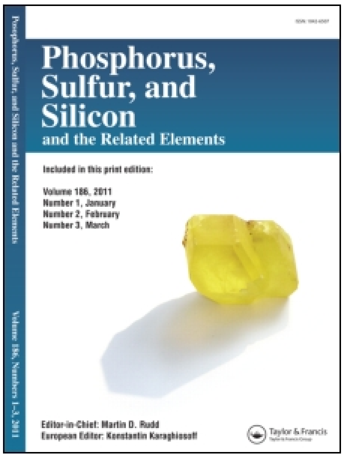

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Structure-Reactivity Relationship in Silacycloalkyl Diamide Complexes of Titanium(IV)

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The structure-reactivity relationship of titanium complexes $CySi(HNBu^t)_2TiCl_2$ (**1**) (*Cy*Si = silacyclobutane, silacyclopentane, silacyclopentene, and silacyclohexane) stabilized by a series of cyclic silyldiamide ligands has been studied. The crystallographic results establish that steric interactions between the silacycloalkyl and *tert*-butyl groups influence the $C(Bu^t)$-N-Ti angles and, hence, the steric environment at titanium. The compounds **1** were further investigated as potential catalysts for the polymerization of ethylene. While sterically less demanding silacyclobutyl and -pentyl diamide complexes (**1a** and **1b**) exhibit low ethylene polymerization activity (3.9 ~5.8 kg PE $mol_{cat}^{-1}h^{-1}$) in the presence of methylalumoxane, highly puckered silacyclohexyl diamide complex **1c** shows better activity (10 kg PE mol_{cat}^{-1} h^{-1}) for the ethylene polymerization when it is activated with MAO.

Keywords: Cyclic silyldiamide; silacycloalkane; titanium; ethylene polymerization

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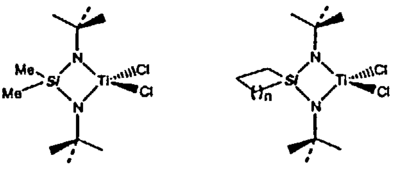
INTRODUCTION

Bidentate diamide ligand with silyl substituent [1] is of considerable interest as ligand in the coordination chemistry of main group elements [2] and transition metals [3]. Such a complex is also attractive as "open" chelating diamide ligand for the synthesis of olefin polymerization precatalysts [4]. In this context, recent reports describing the use of zirconium-diamide complexes $[\{Me_2Si(NBu^t)_2\}ZrR]^+$ for alkene and alkyne insertion are noteworthy [5]. In order to extend this structure-reactivity method for the preparation of silyldiamides, we are exploring the reactivity of Si-functionalized cyclic silyldiamides of varying sizes towards titanium metal. Because the two amide groups should ideally dispose a restricted wedgelike opening, the large and rigid cyclic silyldiamide would seem well-suited as supporting ligands for early transition metals. One important aspect of our work on cyclic silyldiamide complexes is influence of the Si-*Cy* and $N\text{-}Bu^t$ substituents on the steric environment at titanium center. Therefore, through modification of the organic substituents at the bridge silicon position there is the potential for making rational modifications that can be turned to stabilize desired structural and reactivity characterics.



A 1

FIGURE 1. Drawings of siladiazatitanacyclobutane complexes A and 1

RESULT AND DISCUSSIONS

Structural Features of Complexes 1

The values of cyclic silyldiamides studied are very similar, and it seems that the bond lengths and angles associated with siladiazatitanacyclobutane rings in 1 are not significantly affected by effects of sterical crowding driven by exocyclic silacycloalkyl groups. Overall, the four structures are tetrahedral with a planar conformation for the diamido-titanium ring, similar to what is observed in complex A

(Table 1) [6].

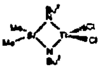
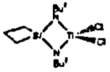
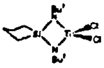
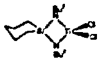
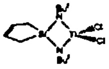
	A	1a	1b	1c	1d
					
Ti-N(Å)	1.829	1.832	1.830	1.833	1.824
Ti-Cl(Å)	2.250	2.250	2.253	2.250	2.239
Si-N(Å)	1.766	1.759	1.772	1.778	1.759
N-Ti-N(°)		85.18	85.61	85.8	85.1
Cl-Ti-Cl(°)	96.89	112.51	111.40	112.6	112.0
N-Si-N(°)		89.64	89.15	89.1	89.1
C-Si-C(°)	97.3	81.4	96.9	105.6	96.5

TABLE 1. Comparison of important structure parameters of 1

Comparison of important structure parameters in Table 1 shows that the Ti-Cl bond lengths (2.239 Å average) in **1d** are substantially shorter than those of **1a**-**c**, demonstrating the higher electrophilicity of the titanium center. Similarly, the Ti-N bond lengths (1.824 Å average) in **1d** are relatively short, indicating significant N-Ti π-donation character to the bonding. The somewhat 'open' and 'closed' Cl-Ti-Cl and N-Ti-N angles (112.13 and 85.42°, respectively) presumably reflect the constraint on the geometry provided by the *Cy*Si link of the diamide ligand. The Cl-Ti-Cl angle of **1** is significantly larger, by about 10°, than the corresponding angle in Cp_2TiCl_2 (94.5°) and much closer to the ideal tetrahedral value. This opening of the Cl-Ti-Cl angle in these cyclic silyldiamide complexes **1** is likely an indication of lesser steric crowding in the equatorial plane of these compounds. A striking feature, however, is the large variation of the C-Si-C angles in complexes **1**, caused by strain introduced by the silacycloalkane or –alkene ring. The C-Si-C angle in **1a** is 24.2° smaller than that in the corresponding silacyclohexyl-bridged analogue **1c**, and cause an increased stereorigidity in the molecule.

Structure and Catalytic Activity of Complex 1

While the gross structural features of **1** correlate well as shown in Table 1, closer inspection reveals some interesting differences among the four complexes. As expected the silacyclic linkage moiety of the diamide ligands has considerable influence on the structure of titanium dichloride complexes. For easy comparison, the structural features of *spiro*-siladiazatitanacyclobutane rings in **1** are schematically represented (FIGURE 2).

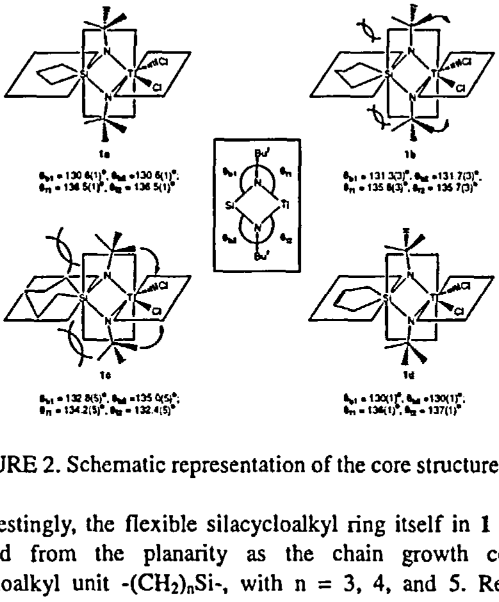


FIGURE 2. Schematic representation of the core structures of 1

Interestingly, the flexible silacycloalkyl ring itself in **1** is gradually distorted from the planarity as the chain growth continues in silacycloalkyl unit -$(CH_2)_nSi$-, with n = 3, 4, and 5. Replacing the methyl substituents at the central silicon atom with a cyclobutyl group has a minimal steric effect on the structure of the metallacycle core. The planar arrangement about silicon is retained and the alkyl substituents remain in the plane of the sillacycle in **1a**. In contrast, the slightly puckered five-membered silacyclopentyl ring is formed in **1b**. Therefore, two *tert*-butyl groups on nitrogens are directed away from this silacyclopentyl ring pointing the opposite directions to reduce steric crowding. For **1c**, the chelate ring is isostructural to that of **1b**, except that the steric demand of the highly puckered six-membered silacyclohexyl ring makes two *tert*-butyl groups on nitrogens project more significantly toward the titanium center.

As might be anticipated, based on the fact that the silacyclohexyl unit is likely sterically more demanding than silacyclobutyl or –pentyl group, the angles around the N atoms show variations that correspond with the steric interactions within the ligand (FIGURE 2). For example, the increase in the Si-N-C(Bu^t) angles (θ_b) and concomitant decrease in the C(Bu^t)-N-Ti angles (θ_f) for **1c** relative to **1a** and **1b** is presumably due principally to steric interactions. In fact, the primary effect of replacing methyl groups at the central silicon with silacycloalkyl group is a change in the C(Bu^t)-N-Ti angle in **1**. The average C(Bu^t)-N-Ti angles (θ_f) in **1a** (136.5°) are comparable to those of Complex A (136.1°). The average C(Bu^t)-N-Ti angles (θ_f) in **1b** (135.8°) and **1c** (133.3°) are 0.3° and 2.8° smaller than those of Complex A (136.1°), respectively.

In particular, increasing the Si-N-Bu^t angle driven by steric interaction of silacyclohexyl group causes the N-Bu^t substituents to project more toward the metal center, in effect protecting the titanium center. We believe that the increased bulkiness of the ancillary silacyclohexyl ligand backbone facilitates the formation of the active catalyst and/or an olefin binding to the titanium center. In fact, the increased bulkiness of **1c** around nitrogen atoms elevates the catalytic activity in comparison with **1a**, but the activity is still significantly lower than that of Cp_2TiCl_2. Similar control of steric crowding at the metal center has been observed in bulky amidinate complexes of aluminum[7], gallium [8], and tin [9].

Entry	Catalyst	[cat.](μmol)	Time(min)	Act.^{b}
1	**3a**	10	30	3.93
2	**3b**	10	30	5.76
3	**3c**	10	30	10.34
4	**3d**	10	30	18.76
5	$Cp_2TiCl_2{}^c$	12	10	323.00

^{a} MMAO-4 (Al:M=1000:1), 70ml of Hexane, 40℃, 1 atm of ethylene.
^{b} kg PE/mol_{cat} h atm. ^{c} 100ml of Hexane.

TABLE 2. Polymerization of ethylene catalyzed by **1**/MMAO

The higher activity of the silacyclopentenyl complex **1d** is probably due to the electron-withdrawing effect of this Si-bridged ligand backbone. The Lewis acidity of the central metal will be increased by the silacyclopentenyl unit pulling electron density through the nitrogen-titanium bond. Such an electron deficiency around titanium center has been well manifested by the unusually short Ti-N and Ti-Cl bonds in the structure of **1d** (Table 1). Therefore, it is this property of the silacyclopentenyl functionality which can be considered as driving force in ethylene polymerization with this complex **1d**. Besides this effect of lowering the electron density at the central metal, silacyclopentenyl unit has a stabilizing effect on the whole molecule.

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