

New Types of Constrained Geometry Catalysts Containing Silacycloalkyl Bridging Unit: Synthesis, Structure, and Polymerization Activity

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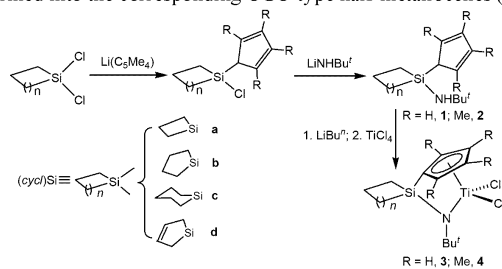
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Introduction

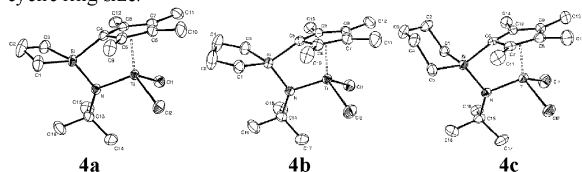
We have recently demonstrated that ansa-metalocene type titanium(IV) complexes of the type (cycl)SiCp₂TiCl₂ with silacycloalkyl-bridged ligands display variable conformational rigidity depending on the size of the ring.¹ Possessing a silacycloalkyl bridge, the exo-cyclic ring can influence the metal center, greatly affecting its catalytic activity. Further developed model of such derivatives would be the constrained geometry complexes (CGC) **3-4** comprising rigid silacycloalkyl group incorporated into the bridging position between cyclopentadienyl and amido functionalities. Variation of exo-cyclic ring size on bridge-head silacycloalkyl unit is likely influential to the catalytic activities of olefin polymerization.

Experimental

Bridged silacycloalkyl amido cyclopentadienes (**1-2**) were prepared by condensation of lithium cyclopentadiene and amine with appropriate silacycloalkyldichlorides. Dilithium salts of **1-2** were subsequently transformed into the corresponding CGC-type half-metallocenes (**3-4**).



Structures of **4a-c** has been confirmed by X-ray analysis. In all three complexes the titanium atom is pseudo-tetrahedrally coordinated by the Cp and amido groups of the CGC-type silacycloalkyl ligand and the two-chloro ligands. Overall the molecular parameters about the central metal atom are comparable to those reported for non-cyclic Dow CGC complex. It is worthy to note that gross geometrical features associated with central titanium metal are similar to each other regardless of exo-cyclic ring size.



Results and Discussion

The results of the polymerization of ethylene using **4**/modified methylaluminoxane (mMAO) are shown in Table 1. It has also been noted that the activity of **4** increases with increasing size of the silacycloalkyl bridge and reaches the maximum in six-membered silacyclohexyl-bridged CGC complex **4c** (9.9×10^3 kg PE mol_{cat}⁻¹ h⁻¹). It is noteworthy that conformation of silacycloalkanes gave rise to

Table 1. Results of ethylene homopolymerization at high temperature^a

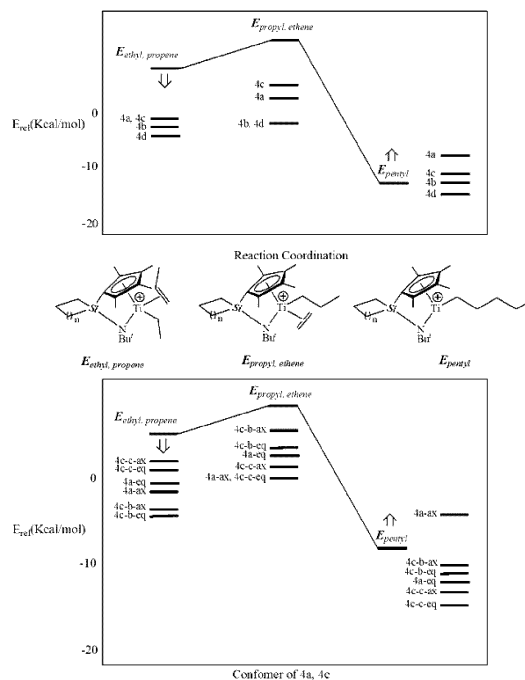
Catalyst	Cocatalyst	Scavenger	Initiation Temp (°C)	ΔT ^b (°C)	Activity ^c	M _w × 10 ^{-4d}	M _w /M _n ^d
4a	Ph ₃ CB(C ₆ F ₅) ₄	mMAO	140	12	6.0	41.8	3.0
4b	Ph ₃ CB(C ₆ F ₅) ₄	mMAO	140	16	7.3	31.2	2.6
4c	Ph ₃ CB(C ₆ F ₅) ₄	mMAO	140	17	9.9	32.7	3.3
4d	Ph ₃ CB(C ₆ F ₅) ₄	mMAO	140	13	6.7	39.2	2.8
(C ₃ Me ₄)-(C ₂ H ₆)Si-NBUtTiCl ₂	Ph ₃ CB(C ₆ F ₅) ₄	mMAO	140	15	8.7	40.4	2.9

^aPolymerization condition: semi-batch type 500 mL autoclave reactor, solvent = cyclohexane, ethylene pressure = 30 kg/Cm², total solution volume = 300 mL, catalyst concentration = 3.3 μM, [catalyst]:[cocatalyst]:[scavenger] = 1: 1.5 : 100, reaction time = 10 min, ^bΔT = T_{maximum} - T_{initial}, ^c×10³ kg of polymer/(mol of Ti·h); ^dWeight average molecular weight (g/mol) and molecular weight distribution measured by PL210 GPC at 135 °C

enhanced catalytic activity of the titanium center although the cyclic ring and titanium center are far remoted from each other. To obtain some information on the effect of silacycloalkyl ring, DFT calculation was performed and their energy profiles were examined.

As for the model system, the "real" cationic metal(IV) alkyl complex is a metal-propyl ethene complex (Figure 1, center) that is higher in energy than a metal-ethyl propene complex (Figure 1, left) and higher than a metal-pentyl complex (Figure 1, right). Increasing the ring size is seen to accelerate the formation of the insertion precursor pentyl complex, whereas termination becomes less favorable since the energy level of the ethyl propene complex is rising. Therefore, more favorable formation of pentyl complex and less favorable formation of ethyl propene complex should give a catalyst better activity.

Figure 1. Results of DFT calculation



Conclusions

The bulky silacycloalkyl bridge of the ligand form a rather wide gap in the equatorial plane of the complexes that may allow selective access of substrate molecules to the Lewis-acidic metal centers. Therefore, we have prepared and structurally characterized a series of silacycloalkyl bridged CGC-type complexes **3-4**, demonstrating the utility of silacycloalkyl amido-pentadienyl as potential catalysts for the polymerization of ethylene.

Reference

[1] Kim, S.-J.; Lee, Y.-J.; Kang, E.; Kim, S. H.; Ko, J.; Lee, B.; Cheong, M.; Suh, I.-H.; Kang, S. O. *Organometallics* **2003**, *22*, 3958.