

Construction of *Ortho*-Phenylene-Bridged Cp/Amido Titanium Complexes and Their Ethylene/ α -Olefin Copolymerizations

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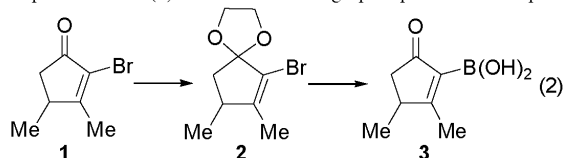
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Introduction

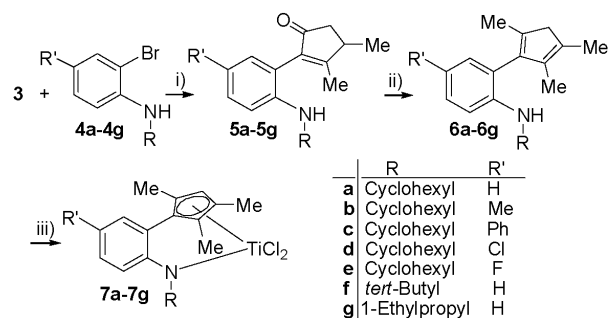
The silylene bridged Cp/amido complexes of group 4, which are called as CGC (constrained geometry catalyst), have received considerable attention.¹ Advantages of the CGC over the conventional biscyclopentadienyl metallocene catalysts are thermal stability, high α -olefin incorporation, and high molecular weight in the ethylene/ α -olefin copolymerizations, which enable its use in a commercial process. Various successful modifications on the standard CGC, $[\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{Cp})(\text{N}^i\text{Bu})]\text{TiCl}_2$, have been achieved by replacement of the Me_4Cp unit with other π -donor ligands,² but modifications on the bridge unit have not been so successful. Herein, we report a novel preparation route for *ortho*-phenylene-bridged Cp/amido titanium complexes and their ethylene/1-hexene copolymerizations.

Results and discussion

A new synthetic strategy was devised by using the Suzuki-coupling reaction (Scheme 1). The starting material in this route, boronic acid **3**, is prepared in 30 g-scale from 2-bromo-3,4-dimethyl-2-cyclopenten-1-one (**1**) without chromatographic purification steps.



The boronic acid **3** is an excellent substrate for the Suzuki-coupling reaction and the cyclopentenone compounds **5a-5g** are afforded in 88-98% yields when **3** is reacted with 4- R' -2-Br- $C_6H_3N(H)R$ ($R = -C_6H_{11}$, $-CMe_3$, $-CH(CH_2CH_3)_2$; $R' = H$, Me, Ph, Cl, F) under the conventional Suzuki-coupling reaction condition. The cyclopentenone unit is transformed to the trimethylcyclopentadiene unit by the CeCl_3 -mediated carbonyl attack of MeLi followed by H_2O -elimination in acidic work-up.⁷ Reaction of $\text{Ti}(\text{NMe}_2)_4$ with the cyclopentadiene compounds **6a-6g** in benzene at 80 °C affords the desired chelated bis(dimethylamido)titanium complexes which are cleanly converted to the dichlorotitanium complexes **7a-7g** by the treatment of Me_2SiCl_2 . The ^1H and ^{13}C NMR spectra of **7a-7g** are in agreement with the structures. The three Cp- CH_3 signals and one Cp-H signal are observed at 1.5-2.2 ppm and 6.0-6.2 ppm, respectively, as singlets in the ^1H NMR spectra (C_6D_6).



Molecular structure of **7a** is confirmed by the X-ray crystallography (Figure 1). The Cp(centroid)-Ti-N angle has been used as a qualitative measure for the "constrained geometry". The smaller the angle is, the pronounced the "constrained geometry" features should be. The Cp(centroid)-Ti-N angle (104.8 and 104.6°) is smaller than that observed for the standard CGC (107.6°) indicating more constrained feature in **7a**. Metrical parameters show that the constrained feature is more pronounced in this system but the

elements constituting the chelation are not situated in a severely strained position.

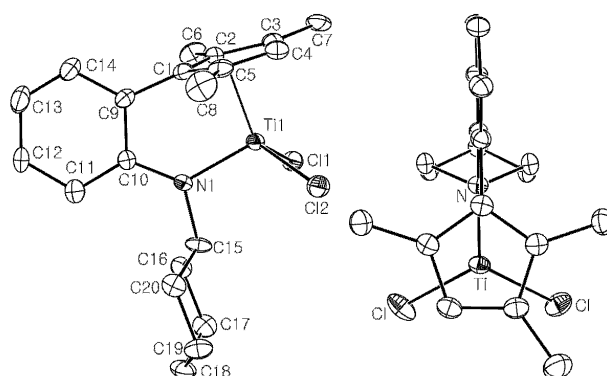


Figure 1. Thermal ellipsoid plot of **7a**

The newly prepared complexes **7a-7g**, after activated with $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in the presence of excess $\text{Al}(\text{iBu})_3$, are tested for ethylene/1-hexene copolymerization (Table 1). The *tert*-butylamido complex **7f** shows low activity but the activities are increased by replacing the *tert*-butyl group with a secondary alkyl such as $(\text{CH}_2\text{CH}_2)_2\text{CH}$ - (**7g**) or cyclohexyl (**7a**). Activities are further increased by attaching some substituents on the phenylene bridge (entries 2-5). The *tert*-butylamido complex **7f** is inferior in terms of 1-hexene incorporation to give nearly linear polyethylene (melting point of the polymer, 125 °C) but cyclohexylamido complex **7a** is capable of incorporating higher amount of 1-hexene than the CGC (17 mol% versus 15 mol% 1-hexene content). The 1-hexene incorporation ability is almost invariant by changing the substituent on the phenylene-bridge (entries 2-5) but substituent effect on the amido group is dramatic. 1-Ethylpropylamido complex **7g** is excellent in incorporation of 1-hexene (22 and 24 mol% of 1-hexene content, respectively). Molecular weights of all the polymers are higher than that of the polymer obtained by the CGC.

Table 1. Ethylene/1-Hexene Copolymerization Results

entry	Complex	Activity ^b	[Hex] ^c (mol%)	M_w	M_w/M_n
1	7a	5.6	17	162000	3.0
2	7b	14	17	145000	2.8
3	7c	15	17	161000	3.0
4	7d	11	17	171000	3.0
5	7e	12	17	151000	2.9
6	7f	1.8	n.d.	142000	3.2
7	7g	8.8	22	174000	3.3
8	CGC ^d	12	15	113000	2.6

^aPolymerization conditions: 30 mL toluene solution of 1-hexene (0.3 M), 0.50 μmol Ti, 2.0 μmol of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, 0.200 mmol of $\text{Al}(\text{iBu})_3$, 60 psig ethylene, 90 °C, 5 minutes. ^bUnit of 10^6 g/molTi·h. ^c1-Hexene content in the copolymer determined by the NMR. ^d $[\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{Cp})(\text{N}^i\text{Bu})]\text{TiCl}_2$.

Conclusions

A Suzuki-coupling route is developed for preparation of *ortho*-phenylene-bridged Cp/amido complexes, one of which shows higher activity, higher 1-hexene incorporation, and higher molecular weight than the silylene-bridged standard CGC $[\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{Cp})(\text{N}^i\text{Bu})]\text{TiCl}_2$.

References

- [1] Cho, D. J.; Wu, C.J.; S, S.; Han, W.-S.; Kang, S. w.; Lee, B. Y. *Organometallics* **2006**, 25, 2133.
- [2] Cho, D. J.; Wu, C.J.; Bok, T.; Lee, E. J.; Lee, C. H.; Han, W.-S.; Kang, S. w.; Lee, B. Y. *Dalton Trans.* 2006, in press.