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o-Phenylene-Bridged Cp/Amido Titanium Complexes for Ethylene/1-Hexene Copolymerizations

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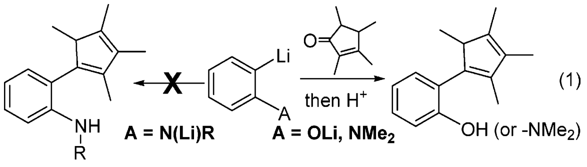
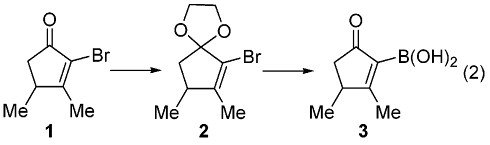
Summary: o-Phenylene-bridged Me_3Cp/amido titanium complexes have been prepared via the Suzuki coupling reaction. Some of them show reactivity comparable to that of the CGC $[Me_2Si(\eta^5\text{-}Me_4Cp)(N^tBu)]TiCl_2$ in ethylene/1-hexene copolymerization in terms of activity, molecular weight, and comonomer incorporation.

The silylene-bridged Cp/amido complexes of group 4, which are called constrained-geometry catalysts (CGC's), have received considerable attention.[1] Advantages of the CGC's over the conventional bis(cyclopentadienyl) 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, $[Me_2Si(\eta^5\text{-}Me_4Cp)(N^tBu)]TiCl_2$, 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. Erker reported the preparation of alkylidene (R^1R^2C)- or vinylidene ($H_2C{=}C$)-bridged Cp/amido complexes, but their activities for ethylene polymerization are significantly lower than that of the standard CGC.[3] The ethylene-bridged complex $[(\eta^5\text{-}Me_4Cp)CH_2CH_2(N^tBu)]TiCl_2$ was prepared, but it showed much lower α-olefin incorporation.[4] Herein, we report a novel preparation route for *o*-phenylene-bridged Cp/amido titanium complexes and their use in ethylene/1-hexene copolymerizations.

Conventionally, aryl-substituted cyclopentadienyl ligands have been prepared by nucleophilic attack of an aryllithium compound at a 2-cyclopentenone derivative and subsequent acid-catalyzed H_2O elimination. Actually, *o*-$C_6H_4(C_5Me_4H)OH$ and *o*-$C_6H_4(C_5Me_4H)NMe_2$ were prepared by this route in moderate yields (eq 1).[5] Attempts to prepare the ligands for *o*-phenylene-bridged Cp/amido complexes by the same strategy using a dilithium compound, $2\text{-}LiC_6H_4(NLiC({=}O)tBu)$,[6] was unsuccessful (eq 1). We attributed this failure to the strong basicity of the amide anion, which triggers deprotonation, instead of the carbonyl attack of the carbon nucleophile at a protic hydrogen on the 2-cyclopentenone.



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 on a 30 g scale from 2-bromo-3,4-dimethyl-2-cyclopenten-1-one (**1**) without chromatographic purification steps (eq 2; see the Supporting Information).



The boronic acid **3** is an excellent substrate for the Suzuki coupling reaction, and the cyclopentenone compounds **5a**−**g** 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 conditions. The cyclopentenone unit is transformed to the trimethylcyclopentadiene unit by the $CeCl_3$-mediated carbonyl attack of MeLi followed by H_2O elimination on acidic workup.[7] Reaction of $Ti(NMe_2)_4$ with the cyclopentadiene compounds **6a**−**g** in benzene at 80 °C affords the desired chelated bis(dimethylamido)titanium complexes, which are cleanly converted to the dichlorotitanium complexes **7a**−**g** by the treatment of Me_2SiCl_2. The ^1H and ^{13}C NMR spectra of **7a**−**g** are in agreement with the structures. The three Cp CH_3 signals and one Cp H signal are observed at 1.5−2.2 and 6.0−6.2 ppm, respectively, as singlets in the ^1H NMR spectra (C_6D_6).

By using the same synthetic strategy, complex **8** is also prepared from the corresponding bromo compound, where one

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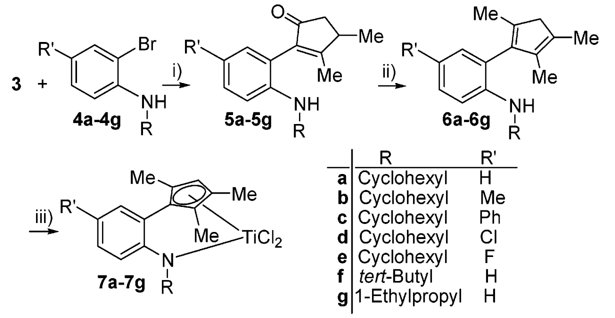
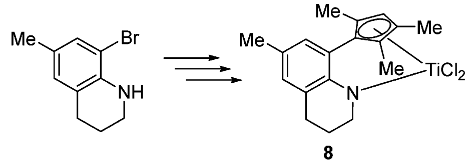
Scheme 1[a]



[a] Legend: (i) Na_2CO_3, $Pd(PPh_3)_4$ (2 mol %); (ii) MeLi/$CeCl_3$, then HCl (2 N); (iii) $Ti(NMe_2)_4$, then Me_2SiCl_2.

can expect a highly opened reaction site (see the Supporting Information).



(3)

The molecular structure of **7a** has been confirmed by X-ray crystallography (Figure 1). Two independent molecules are present in the asymmetric unit cell. The Cp(centroid)−Ti−N angle has been used as a qualitative measure for the “constrained geometry”. The smaller the angle is, the more 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 features in **7a**.[8] The ipso carbon on the phenylene bridge (C(9)) does not severely deviate from the cyclopentadienyl plane (Cp(centroid)−C(1)−C(9) angle 170.6°), which is in contrast with the observation of severe deviation of the Si atom from the cyclopentadienyl plane for the silylene-bridged complexes (Cp(centroid)−C(bridgehead)−Si angles for $C_5R_4SiMe_2$(N-*t*-Bu) titanium complexes 150−154°).[8] The C(1)−C(9)−C(10) angle (113.36(13) and 113.67(14)°) and the N−C(10)−C(9) angle (113.18(13) and 112.95(14)°) are not abnormal. Overall, the constrained features are more pronounced in this system but the elements constituting the chelation are not situated in severely strained positions. The Ti−N bond distance (1.9003(13) and 1.9027(13) Å) is slightly shorter than that observed for the standard CGC (1.907(4) Å). The nitrogen atom is perfectly trigonal (sum of the bond angle around the nitrogen atom 360.0°). The molecular structure of **7d** was also confirmed by X-ray crystallography (Supporting Information). The geometrical parameters are similar to those observed for **7a** (Cp(centroid)−Ti−N angle 105.0°).

The newly prepared complexes **7a**−**g** and **8**, after activation with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in the presence of excess $Al(^iBu)_3$, have been 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 $(CH_3CH_2)_2CH-$ (**7g**) or cyclohexyl (**7a**). Activities are further increased by attaching some substituents on the phenylene bridge (entries 2−5). Interestingly, complex **8** shows an activity almost two times higher than that of the CGC.

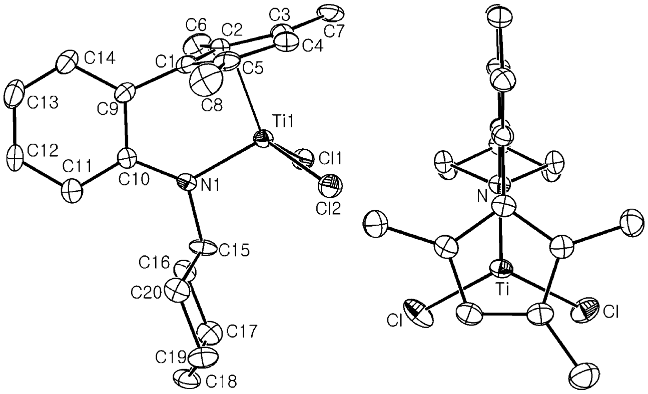


Figure 1. Thermal ellipsoid plot (30% probability level) of **7a** (side and top views, hydrogens omitted). Selected bond distances (Å) and angles (°): Ti−Cp(centroid), 2.008; Ti(1)−Cl(1), 2.2944(7); Ti(1)−Cl(2), 2.2889(7); Cl(2)−Ti(1)−Cl(1), 105.52(2); C(15)−N(1)−Ti(1), 107.67(9); C(10)−N(1)−Ti(1), 129.11(10); C(10)−N(1)−C(15), 123.21(12).

Table 1. Ethylene/1-Hexene Copolymerization Results[a]

entry	catalyst	activity (10^6 g/((mol of Ti) h))	[Hex][b] (mol %)	M_w	M_w/M_n
1	**7a**	5.6	17	162 000	3.0
2	**7b**	14	17	145 000	2.8
3	**7c**	15	17	161 000	3.0
4	**7d**	11	17	171 000	3.0
5	**7e**	12	17	151 000	2.9
6	**7f**	1.8	n.d.	142 000	3.2
7	**7g**	8.8	22	174 000	3.3
8	**8**	21	24	81 000	2.3
9	CGC[c]	12	15	113 000	2.6

[a] Polymerization conditions: 30 mL of a toluene solution of 1-hexene (0.3 M), 0.50 μmol of Ti, 2.0 μmol of $[Ph_3C][B(C_6F_5)_4]$, 0.200 mmol of $Al(^iBu)_3$, 60 psig of ethylene, 90 °C, 5 min. [b] 1-Hexene content in the copolymer determined by the ^1H NMR spectra. [c] $[Me_2Si(\eta^5\text{-}Me_4Cp)(N^tBu)]TiCl_2$.

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 the cyclohexylamido complex **7a** is capable of incorporating a greater amount of 1-hexene than can the CGC (17 mol % versus 15 mol % 1-hexene content). The 1-hexene incorporation ability is almost invariant on changing the substituent on the phenylene bridge (entries 2−5), but the substituent effect on the amido group is dramatic. The (1-ethylpropyl)amido complex **7g** and fused-ring complex **8** are excellent in the incorporation of 1-hexene (22 and 24 mol % of 1-hexene content, respectively). Molecular weights of all the polymers except that obtained by **8** are higher than that of the polymer obtained by the CGC.

Conclusively, a Suzuki coupling route has been developed for the preparation of *o*-phenylene-bridged Cp/amido complexes. Some of them show higher activity, higher 1-hexene incorporation, and higher molecular weight than the silylene-bridged standard CGC $[Me_2Si(\eta^5\text{-}Me_4Cp)(N^tBu)]TiCl_2$. Further derivatization using this route is currently under study.

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Supporting Information Available: Text giving details of the syntheses and characterizations of all new compounds and polymerization details and CIF files giving crystallographic data for **7a**,**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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