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Ethylene trimerization with a half-sandwich titanium complex bearing a pendant thienyl group†

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A half-sandwich titanium complex with a pendant thienyl group, activated by methylalumoxane (MAO), can trimerize ethylene to 1-hexene with considerable activity and high selectivity; the coodination of the sulfur atom to the titanium center is proposed to be responsible for the selective trimerization of ethylene.

1-Hexene, which is used as a comonomer for synthesis of linear low-density polyethylene (LLPDE), can be produced by catalytic trimerization of ethylene. Presently, most catalytic trimerization systems are based on chromium compounds.[1] To find an alternative catalyst system based on other metals is of academic and industrial interest. Hessen and co-workers reported that titanium complexes with an arene-pendant cyclopentadienyl ligand in combination with methylalumoxane (MAO) can selectively trimerize ethylene with high activity.[2] The arene-pendant cyclopentadienyl ligand is likely to exhibit hemilabile behavior, stabilizing the titanium center of the activated species by η^6 coordination and slipping to make room for the incoming ethylene.

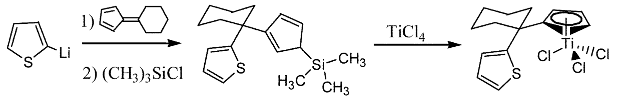
Modification of the Cp ring by introducing a pendant group that has the ability to coordinate to a metal center is of current interest. All kinds of ligands such as alkenyl, phenyl, alkoxyl, O-donor, N-donor, and P-donor groups have attracted much attention.[3] However, less attention has been paid to S-donor ligands.[3d]

Thiophene is a special ligand. In contrast to dialkyl sulfides, thiophene is a weak S-donor, so it can be expected to only weakly coordinate to metal centers.[4] Furthermore, as an electron-rich aromatic system, thiophene can coordinate to metal centers by η^5 coordination.[5] If we introduce the thiophene moiety into a cyclopentadienyl ring, it is envisaged that the thiophene-cyclopentadienyl ligand may serve as a hemilabile ligand in the catalytic trimerization of ethylene. With this in mind, we designed and synthesized a titanium complex with a thiophene-pendant cyclopentadienyl ligand, complex **1**‡ (Scheme 1).

In complex **1**, the thiophene moiety is linked to the Cp ring through a carbon bridge at the 2-position.

Complex **1** with MAO was tested in ethylene conversion. The results are listed in Table 1.

From the results shown in Table 1, as we expected, **1**/MAO exhibits considerable activity as well as high selectivity for ethylene trimerization. In addition to 1-hexene, a small amount of butene (2–3 wt%) is produced. No other oligomers such as C_8 and C_{10} olefins are detected. In most cases, polymer is produced. The highest activity for trimerization is 220 Kg mol^{-1} Ti h^{-1} (under 8 atm of ethylene pressure and at 30 °C).



Scheme 1

It is noted that the selectivity of the catalyst is temperature-dependent. At 0 °C, only a trace of polymer is produced and the selectivity is very high (95%), but when we increase the reaction temperature, although the activity for trimerization is retained, the selectivity decreases dramatically because the amount of polymer increases. It is interesting that, when the temperature is raised to 80 °C, **1**/MAO shows considerable activity not only for trimerization but also for polymerization.

The MAO activated half-sandwich titanium complex has been shown to be a multisite system containing Ti(IV), Ti(III) and Ti(II) species.[6] The Ti(II) species was proposed to be the initial active species for the trimerization of ethylene.[7] Hessen elucidated that the pendant arene group may promote the formation of the titanium(II) species and provide it with additional stability.[2] In our case, the thiophene moiety could coordinate to the titanium center when complex **1** is activated by MAO, and this coordination may also make the formation of the titanium(II) species much more favourable, which leads to the highly selective trimerization of ethylene. But at high temperatures, the thiophene partly dissociates from the titanium center, so the selectivity of 1-hexene decreases.

As mentioned above, thiophene can coordinate to the metal center by two modes, η^1-S coordination and η^5 coordination. In the **1**/MAO catalyst system, the two coordination modes are both favourable with respect to molecular structure. Our attention was focused on clarifying which of the two coordination modes is essential for ethylene trimerization. In order to obtain some evidence, we synthesized complex **2** (Scheme 2).

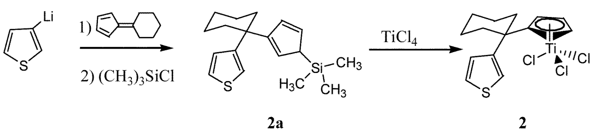
In complex **2**, the thiophene moiety is linked to the Cp ring through a carbon bridge at the 3-position, thus, the sulfur atom is away from the titanium center, which makes it impossible for the sulfur atom to coordinate to the titanium center. However in complex **2**, the possibility of η^5-coordination still exists. We studied the catalytic behavior of **2** in combination with MAO in ethylene conversion, compared with **1**/MAO. The results are shown in Table 2.

Entries 1 and 2 describe the catalytic behavior of **2**/MAO. In **2**/MAO, polymer is produced as the major product and the

Table 1 Results of ethylene conversion with **1**/MAO[a]

Entry	T/°C	Pressure/ atm	1-Hexene/g	Polymer/g	Productivity[b] of 1-hexene	Selectivity of 1-hexene (wt%)
1	0	5	0.090	Trace	120	> 95
2	30	5	0.117	0.017	156	84
3	80	5	0.102	0.206	136	33
4	30	8	0.165	0.022	220	86

[a] Reaction conditions: 1.5 μmol catalyst; Al : Ti = 1000 : 1; 20 ml toluene solvent; 30 min run time. [b] In Kg mol^{-1} Ti h^{-1}.



2a

2

Scheme 2

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† Electronic supplementary information (ESI) available: syntheses of compounds **1** and **2**. See http://www.rsc.org/suppdata/cc/b3/b309749h/

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Table 2 Results of ethylene conversion with **2**/MAO, compared with **1**/MAO[a]

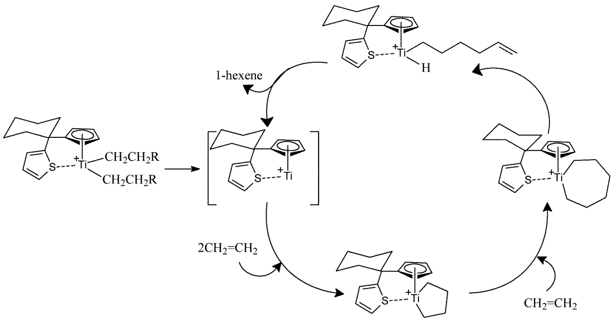
Entry	Complex	T/°C	1-Hexene/g	Polymer/g	Productivity[b] of 1-hexene	Selectivity of 1-hexene (wt%)
1	**2**	0	0.009	0.040	12	18
2	**2**	30	0.014	0.094	19	12
3	**1**	0	0.090	Trace	120	> 95
4	**1**	30	0.117	0.017	156	84

[a] Reaction conditions: 1.5 μmol catalyst; Al : Ti = 1000 : 1; 5 atm ethylene pressure; 20 ml toluene solvent; 30 min run time. [b] In Kg mol^{-1} Ti h^{-1}.

activity with respect to trimerization is low. The fact that the catalytic behavior of **2**/MAO dramatically differs from that of **1**/MAO indicates that it is not the η^5 coordination mode but the η^1-S coordination mode that plays an important role in ethylene trimerization. Very recently, Bianchini and co-workers reported that Co(II) complexes with pyridinimine ligands bearing a thienyl group can serve as efficient catalysts for oligomerization of ethylene.[8] They suggested that the sulfur atom would be likely to play an active role during the oligomerization of ethylene. While in our case, by comparing the catalytic behavior of **1**/MAO and **2**/MAO, a further conclusion can be drawn that the coordination of the sulfur atom to the titanium center plays an important role during the trimerization of ethylene.

Hessen proposed a mechanism involving titanacycle intermediates accounting for the selective formation of 1-hexene. Recently, a theoretical study of ethylene trimerization at a cationic $(C_6H_5CH_2C_5H_4)$Ti fragment supported this mechanism.[9] By analogy, a possible mechanism proposed in our case is shown in Scheme 3.

In summary, we have found that a titanium complex with a thienyl-cyclopentadienyl ligand can serve as an efficient catalyst precursor for ethylene trimerization. The coordination of the sulfur atom is likely to be essential for the selective trimerization of ethylene. Our findings indicate that σ-donor ligands attached to the cyclopentadienyl ring can also play an important role in ethylene trimerization, which will greatly expand the library of catalysts for ethylene trimerization.



Scheme 3 Proposed mechanism for the formation of 1-hexene.

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Notes and references

‡ Selected data for **1**: ^{1}HNMR (500 MHz, CDCl$_3$) δ 7.25 (m, 1H, α-thiophene-H); δ 7.00 (m, 2H, β-thiophene-H); δ 6.98 (ps t, $^3J_{HH}$ = 2.9 Hz, 2H, Cp–H); δ 6.79 (pst, $^3J_{HH}$ = 2.9 Hz, 2H, Cp–H); δ 2.60 (d, $^2J_{HH}$ = 12.9 Hz, 2H, α-CH$_{eq}$); δ 2.14 (m, 2H, α-CH$_{ax}$); δ 1.66 (br, 3H, β-and γ-CH$_2$); δ 1.27–1.54 (m, 3H, β-and γ-CH$_2$). Anal. $C_{15}H_{17}Cl_3STi$, found (calc) C: 47.28 (46.96) H: 4.49 (4.47).

Selected data for **2**: ^{1}HNMR (500 MHz, CDCl$_3$) δ 7.33 (dd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, α-thiophene-H); δ7.19 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, α-thiophene-H); δ 7.07 (dd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, β-thiophene-H); δ 6.90 (pst, $^3J_{HH}$ = 2.9 Hz, 2H, Cp–H); δ 6.78 (pst, $^3J_{HH}$ = 2.8 Hz, 2H, Cp–H); δ 2.59 (d, $^2J_{HH}$ = 12.9 Hz, 2H, α-CH$_{eq}$); δ 2.03 (m, 2H, α-CH$_{ax}$); δ1.53–1.70 (br, 3H, β-and γ-CH$_2$); δ 1.30–1.44 (m, 3H, β-and γ-CH$_2$). Anal. $C_{15}H_{17}Cl_3STi$, found (calc.) C: 47.00 (46.96) H: 4.61 (4.47).

1 (*a*) J. R. Briggs, *US Pat. Appl.* 4668838, 1987; (*b*) J. R. Briggs, *Chem. Commun.*, 1989, **11**, 674; (*c*) Y. Araki, H. Nakamura, Y. Nanba and T. Okano, *US Pat. Appl.* 5856612, 1997; (*d*) D. F. Wass, *PCT Int. Appl.* WO 0204119, 2002; (*e*) A. Carter, S. A. Cohen, N. A. Cooley, A. Murphy, J. Scutt and D. F. Wass, *Chem. Commun.*, 2002, **8**, 858.
2 (*a*) P. J. W. Deckers, B. Hessen and J. H. Teuben, *Angew. Chem., Int. Ed.*, 2001, **40**, 2516; (*b*) P. J. W. Deckers, B. Hessen and J. H. Teuben, *Organometallics*, 2002, **21**, 5122.
3 (*a*) J. Okuda, *Comments Inorg. Chem.*, 1994, **16**, 185; (*b*) P. Jutiz and U. Siemeling, *J. Organomet. Chem.*, 1995, **500**, 178; (*c*) U. Siemeling, *Chem. Rev.*, 2000, **100**, 1495; (*d*) H. Butenschön, *Chem. Rev.*, 2000, **100**, 1527.
4 (*a*) R. J. Angelici, *Acc. Chem. Res.*, 1988, **21**, 387; (*b*) J. L. Burmeister, *Coord. Chem. Rev.*, 1990, **105**, 77.
5 (*a*) M. F. Balley and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1306; (*b*) J. R. Lockemeyer, T. B. Rauchfuss, A. L. Rheighold and S. R. Wilson, *J. Am. Chem. Soc.*, 1989, **111**, 8828.
6 J. C. W. Chien, Z. Salajka and S. Dong, *Macromolecules*, 1992, **25**, 3199.
7 C. Pellecchia, D. Pappalardo and G. J. Gruter, *Macromolecules*, 1999, **32**, 4491.
8 C. Bianchini, G. Mantovani, A. Meli, F. Migliacci and F. Laschi, *Organometallics*, 2003, **22**, 2545.
9 A. N. J. Blok, P. H. M. Budzelaar and A. W. Gal, *Organometallics*, 2003, **22**, 2564.