Trimerization of Ethylene to 1-Hexene with Titanium Complexes Bearing Phenoxy–Imine Ligands with Pendant Donors Combined with MAO

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Summary: New Ti complexes bearing phenoxy—imine ligands with pendant aryl—OMe donors have been developed for ethylene trimerization to produce 1-hexene. These Ti complexes combined with methylaluminoxane selectively trimerize ethylene to form 1-hexene with exceptionally high activity (e.g., 6.59 tons of 1-hexene/((g of Ti) h)).

Ethylene oligomerization normally results in the formation of a range of α -olefins following a Schulz–Flory distribution. Thus, the development of catalysts capable of selectively forming a desired α -olefin would be of great significance. In particular, the selective trimerization of ethylene to 1-hexene has received a great deal of attention because of the importance of this comonomer in the manufacture of linear low-density polyethylene (LLDPE).¹

Since the first report on Cr-catalyzed selective ethylene trimerization by Manyik and co-workers, a large number of highly active and selective Cr-based catalysts for this conversion have been developed.^{2,3} Additionally, a great deal of effort has been exerted into developing non-Cr-based

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Figure 1. Ti complexes employed in this study.



Figure 2. Molecular structure of complex 3.

catalysts for ethylene trimerization, resulting in the introduction of high-performance catalysts based on a number of transition metals, including Zr,⁴ Ti,⁵ and Ta.⁶

Our research, which is based on a ligand-oriented catalyst design concept, has resulted in the discovery of phenoxy– imine ligated early-transition-metal complexes (aka FI catalysts) for the controlled (co)polymerization of olefinic monomers.⁷ Notably, FI catalysts, after activation, can polymerize ethylene with very high efficiency independent of the central metals employed (Ti, Zr, Hf, V, Cr, etc.), suggesting the significant potential of a phenoxy–imine ligand for efficient ethylene insertion. Therefore, in recent years, there has been increased interest in the further development of FI catalysts and related complexes for the oligomerization/polymerization of ethylene.^{7,8}

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Table 1.	Catalytic	Ethylene	Conversion	with (Complexes 1	1-3 with MAO ^a
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entry		C ₂ H ₄ pressure (MPa)	activity (kg/((g of Ti) h))	selectivity (wt %)			
	complex			C ₆	C ₁₀	PE	l-hexene productivity (kg of l-hexene/((g of Ti) h))
1	1	0.8	5	76.6	0	23.4	4
2	2	0.8	138	86.2	12.2	1.6	119
3	3	0.8	169	91.4	6.4	2.1	155
4^b	3	1.6	654	93.2	5.8	1.0	609
5^b	3	3.2	2720	93.9	5.6	0.5	2550
6^b	3	5.0	7140	92.3	7.3	0.4	6590

^a Conditions: cyclohexane, 30 mL (^b150 mL); complex, 0.5 µmol; MAO, 5.0 mmol as Al; 30 °C; 60 min.

As part of a program to develop new catalysts for olefin insertion based on FI catalysts, we have investigated earlytransition-metal complexes with phenoxy-imine ligands bearing pendant donors. Such research has led to the discovery of Ti complexes incorporating phenoxy-imine ligands with pendant aryl-OMe donors that can selectively transform ethylene to 1-hexene with extremely high productivity, representing the first examples of phenoxy-imine ligated catalysts for selective ethylene trimerization. Therefore, we herein describe the catalytic performance of these Ti complexes.

Shown in Figure 1 are Ti complexes 1-3 used in this study. which incorporate phenoxy-imine ligands with pendant donors (tridentate phenoxy-imine ligands). The tridentate phenoxy-imine ligands were readily synthesized by Schiff base condensations between the corresponding salicylaldehydes and primary amines. Complex formation was achieved by the treatment of the tridentate ligand with $TiCl_4$ (1, 27%; 2, 59%; 3, 82%). The ¹H NMR spectra of complexes 2 and 3 exhibited a pair of singlet peaks assigned to the methyl protons of a cumyl group (complex 2) or AB system peaks derived from the methylene protons of an adamantyl group (complex 3), consistent with the facial coordination of the tridentate ligands. Indeed, an X-ray crystallographic analysis has demonstrated that complex 3 adopts a distorted-octahedral structure with the tridentate phenoxy-imine ligand coordinated in a facial fashion (bond distances: Ti-phenoxy-O = 1.827(2) A, Ti-imine-N = 2.197(3) Å, Ti-aryl-O = 2.182(2) Å) (Figure 2).

The results of catalytic ethylene conversion experiments using complexes 1 and 2 with methylaluminoxane (MAO) under 0.8 MPa of ethylene pressure are given in Table 1 (entries 1 and 2). Complex 1, bearing a pendant aryl–OPh donor, produced 1-hexene (76.6 wt %) displaying low activity along with a considerable amount of PE. To our surprise, however, complex 2, with a pendant OMe donor, after activation yielded a catalyst with much higher selectivity for 1-hexene (86.2 wt %) with extremely high productivity

Scheme 1. Plausible Mechanism for the Formation of 1-Hexene



L: tridentate phenoxy-imine ligand

(119 kg of 1-hexene/((g of Ti) h)). This result indicates that the introduction of the OMe group in place of the OPh group converted a poorly active ethylene trimerization catalyst into a highly active and selective ethylene trimerization catalyst, illustrating how a minor change in the ligand structure can have a dramatic effect on catalyst performance.⁹

A plausible mechanism for the formation of 1-hexene is presented in Scheme 1, which is founded on a metallacyclic mechanism that involves Ti(II) and Ti(IV) species.^{5,10} The mechanism involves the coordination of two ethylene molecules, oxidative coupling to yield a metallacyclopentane, insertion of a third ethylene molecule to form a metallacycloheptane, and β -H elimination/reductive elimination (or concerted 3,7-H transfer) to form 1-hexene.

We postulate that the OMe donor may play a crucial role in the formation and/or stabilization of the Ti(II) species that is presumably the initial active species for ethylene trimerization.^{8b,f,9} Scheme 2 displays a possible mechanism for the formation of the Ti(II) species, which is the key species for the reaction. The mechanism involves the initial formation of a cationic dimethyl Ti(IV) species, insertion of ethylene to form a cationic dialkyl Ti(IV) species, and (a) intramolecular β -H transfer or (b) β -H elimination/reductive elimination to form the Ti(II) species.^{5,10}

Further research on Ti complexes incorporating phenoxyimine ligands with aryl-OMe donors has resulted in the development of complex **3** having an adamantyl group *ortho* to the phenoxy-O. Under 0.8 MPa of ethylene pressure, complex **3** with MAO exhibited higher 1-hexene selectivity (91.4 wt %) and activity (155 kg of 1-hexene/((g of Ti) h)) than

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⁽⁹⁾ DFT calculations suggested that the Ti–OR bond distance of **2** (2.31 Å) is shorter than that of **1** (2.43 Å), which might be responsible for the difference in catalytic performance between the OMe and OPh donors.

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Scheme 2. Possible Mechanism for the Formation of a Ti(II) Species



L: tridentate phenoxy-imine ligand

complex **2** (Table 1, entry 3). Increasing the ethylene pressure to 5.0 MPa gave a significant enhancement of 1-hexene productivity (6.59 tons of 1-hexene/((g of Ti) h), TOF = 3.7×10^6 /h) with higher selectivity (92.3 wt %).¹¹ This activity represents one of the highest values reported to date for ethylene trimerization catalysts. In fact, this activity is 2 orders of magnitude greater than that seen with the commercially employed Cr-based catalyst (Phillips catalyst) under similar ethylene pressure conditions.

Ethylene pressure studies have revealed a second-order dependence of productivity on ethylene pressure (entries 3-6) (see the Supporting Information), which is consistent with the metallacyclic mechanism (Scheme 1).¹⁰ This catalytic behavior may suggest that the rate-determining step is the

formation of the metallacyclopentane species via a pair of coordinated ethylene molecules.

GC-MS together with ¹H and ¹³C NMR studies have suggested that, as byproducts other than PE, branched decenes (cotrimers of the 1-hexene produced with ethylene) were formed, 2-butyl-1-hexene being predominant (ca. 90 wt %). Considering that the formation of 2-butyl-1-hexene is virtually second order in ethylene pressure (entries 3–6), 2-butyl-1-hexene is produced by a 1,2-insertion of 1-hexene into the metallacyclopentane to form a 3-butylmetallacycloheptane, followed by β -H elimination/reductive elimination (or concerted 3,7-H transfer) (see the Supporting Information). Further studies, including a detailed mechanistic investigation, are underway.

In summary, we have developed new Ti complexes for ethylene trimerization to produce 1-hexene, which are supported by phenoxy-imine ligands with pendant aryl-OMe donors (tridentate phenoxy-imine ligands). These complexes combined with MAO can selectively transform ethylene into 1-hexene with unprecedented productivity (e.g., 6.59 tons of 1-hexene/((g of Ti) h)). The results reported herein further demonstrate the unique catalytic behavior of transition-metal complexes incorporating phenoxy-imine-based ligands (FI-type ligands) for ethylene insertion reactions.^{7,8}

Supporting Information Available: Text, figures, and a CIF file giving details of the synthesis of 1-3, crystallographic data for 3, catalytic ethylene conversion experiments, a plausible mechanism for the formation of 2-butyl-1-hexene, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽¹¹⁾ A 1-hexene-rich environment is probably responsible for the 1-hexene selectivity at 5.0 MPa ethylene pressure (92.3 wt %) being lower than that at 3.2 MPa ethylene pressure (93.9 wt %), since the amount of byproduct decenes formed is largely a product of 1-hexene concentration.