silica tubes under an argon atmosphere in a glove box. These tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The sample in the first tube was heated to 823 K at 1.5 K min^{-1}, kept at 823 K for three days, very slowly cooled at 4 K h^{-1} to 423 K, then cooled to room temperature to afford black hexagonal plates of the hexagonal modification in about 80 % yield. The sample in the second tube was heated to 873 K at 1.5 K min^{-1}, kept at 873 K for two days, when the furnace was turned off. Black needles of the orthorhombic modification were obtained in about 70 % yield. The reaction mixtures were washed free of alkali metal chalcogenides with dimethylformamide and then dried with acetone. Analysis of these crystals with an energy-dispersive X-ray (EDX)-equipped Hitachi S-4500 scanning electron microscope showed K/Ba/Ti/S approximately in the ratio 5:1:10:30; the presence of O was observed but could not be quantified.

General crystallographic details: Bruker Smart 1000 CCD diffractometer,[30] graphite-monochromatized Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 153$ K. Data were collected by an ω scan of 0.3° in groups of 606, 606, and 606 frames at ϕ settings of 0°, 120°, and 240° for the hexagonal modification and in groups of 606, 606, 606, and 606 frames at ϕ settings of 0°, 90°, 180°, and 270° for the orthorhombic modification. The exposure times were 15 s frame^{-1}. Intensity data were collected with the program SMART.[30] Cell refinement and data reduction were carried out with the use of the program SAINT,[30] face-indexed absorption corrections were carried out with the program XPREP,[31] and the frame variations were further corrected with the use of the program SADABS.[30] The structures were solved with the direct methods program SHELXS and refined with the least-squares program SHELXL of the SHELXTL-PC suite of programs.[31] The final refinements included anisotropic displacement parameters and a secondary extinction correction. Crystal structure analysis of K$_4$Ba[Ti$_6$OS$_{20}$]: black hexagonal plate, $0.040 \times 0.078 \times 0.084$ mm, hexagonal, $P6_322$, $a = 9.3386(4)$, $c = 18.130(1)$ Å, $V = 1369.3(1)$ Å^3, $T = 153$ K, $Z = 2$, $\rho_{calcd} = 3.004$ g cm^{-3}, $\theta_{max.} = 28.88°$, 11 429 reflections measured, 1175 unique, 1064 observed with $I > 2\sigma(I)$, $\mu = 52.12$ cm^{-1}, min/max transmission $= 0.685/0.816$, $R_1 = 0.0374$, $wR_2 = 0.0895$. Black needle, $0.096 \times 0.112 \times 0.248$ mm, orthorhombic, $Fddd$, $a = 11.106(2)$, $b = 15.338(2)$, $c = 32.265(5)$ Å, $V = 5496.0(13)$ Å^3, $T = 153$ K, $Z = 8$, $\rho_{calcd} = 2.993$ g cm^{-3}, $\theta_{max.} = 28.85°$, 16 008 reflections measured, 1749 unique, 1590 observed with $I > 2\sigma(I)$, $\mu = 51.94$ cm^{-1}, min/max transmission $= 0.459/0.713$, $R_1 = 0.0336$, $wR_2 = 0.0894$.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: $(+49)7247$-808-666; e-mail: crysdata@fiz-karlsruhe. de), on quoting the depository numbers CSD-411697 for the orthorhombic modification and CSD-411698 for the hexagonal modification.

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Switching a Catalyst System from Ethene Polymerization to Ethene Trimerization with a Hemilabile Ancillary Ligand**

Patrick J. W. Deckers, Bart Hessen,* and Jan H. Teuben

The chemistry of transition metal complexes with hemi-labile ancillary ligands (i.e., with multidentate ligands that have a mixture of tightly bound and substitutionally labile functionalities) is enjoying an increasing popularity.[1] These hemilabile ligands can stabilize reactive metal centers by the chelate effect, but keep the metal accessible for substrate molecules by virtue of the substitutionally labile character of one of the functionalities. Examples of such hemilabile ligands include phosphine – ether, cyclopentadienyl – alkene, and phosphine – arene ligands. In some cases, hemilabile ligands were found to influence the selectivity and stability of transition metal catalysts.[2] Here we report that the catalyst system $[(\eta^5$-C$_5$H$_4$CMe$_2$R)TiCl$_3$]/MAO (MAO = methylalum-oxane) is transformed from an ethene polymerization catalyst into an ethene trimerization catalyst, producing 1-hexene, by simply changing the ligand substituent R from a methyl to a

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phenyl group. It appears that the hemilabile behavior of the cyclopentadienyl ligand with a pendant arene group is responsible for this drastic switch in catalyst performance.

The catalyst precursors used in this study, $[(\eta^5\text{-}C_5H_4CMe_2R)TiCl_3]$ (R = Ph, **1**; 3,5-dimethylphenyl, **2**; Me, **3**), are readily obtained by reaction of 6,6-dimethylfulvene with the appropriate RLi reagent followed by reaction with $TiCl_4$, or by reaction of $TiCl_4$ with the corresponding $Me_3Si(C_5H_4CMe_2R)$ reagent.[3, 4] In previous work by us and others it has been shown that cationic dialkyl derivatives of **1** and **2** can be generated by reaction of the trimethyl complexes $[(\eta^5\text{-}C_5H_4CMe_2Ar)TiMe_3]$ with Lewis acids such as $B(C_6F_5)_3$, and that in these cationic species $[(C_5H_4CMe_2Ar)TiMe_2]^+$ the arene moiety is η^6-coordinated to the metal center. For Ar = $3,5\text{-}Me_2C_6H_3$ this yields a relatively stable 16-electron complex that does not polymerize propene at ambient temperature and pressure.[4] For Ar = C_6H_5 the coordination is noticeably weaker, and a modest activity in propene polymerization was reported.[3]

We have now observed that activation of the trichloride **1** with 1000 equiv of the cocatalyst MAO in toluene under ethene pressure generates a catalyst that converts ethene predominantly to 1-hexene. Results of catalytic ethene conversion experiments under various conditions are listed in Table 1. The catalyst produces at ambient temperatures olefin trimerization products with high selectivity (95 – 98 wt %overall). These products consist of two fractions: C_6 products (>99 % 1-hexene) and C_{10} products (cotrimers of

Table 1. Catalytic ethene conversion with the **1**/MAO catalyst system (toluene solvent, 15 μmol Ti, Al:Ti = 1000, 30 min run time).

p(ethene) [bar]	T [°C]	C_6 products [g] (wt %)	C_{10} products [g] (wt %)	PE [g] (wt %)	Productivity[a]
2	30	8.0 (87)	1.0 (11)	0.2 (1.6)	1066
5	30	20.9 (83)	3.5 (14)	0.5 (1.8)	2787
10	30	47.2 (86)	5.1 (9)	1.4 (2.6)	6292
5	50	12.4 (83)	1.6 (11)	0.7 (4.6)	1653
5	80	3.3 (76)	0.2 (4)	0.8 (19)	440

[a] In kg C_6 product per mole Ti and h.

ethene and 1-hexene). The C_{10} fraction consists mainly (>75 %) of 5-methyl-non-1-ene. In addition, some 1-octene (1 wt %) and polyethene (PE, 1 – 3 wt %) is produced. The rate of production of 1-hexene increases with increasing ethene pressure, the C_6 productivity being about 550 – 600 kg per mole Ti, h, and bar over a range of 2 – 10 bar in ethene pressure. The thermal stability of the catalyst is modest, and increasing the reaction temperature decreases the overall catalyst productivity due to catalyst degradation (as seen from the decrease in the ethene uptake rate over the run period) and increases the relative amount of PE produced (see Table 1).

The importance of the pendant arene group on the ancillary ligand for 1-hexene production can be seen by comparing the performance of the three catalyst systems **1** – **3**/MAO (Table 2). Making the pendant arene group more electron-rich by adding methyl substituents significantly diminishes the catalyst activity (but the selectivity for trimerization is retained),

Table 2. Catalytic ethene conversion with the **1** – **3**/MAO catalyst systems (toluene solvent, 5 bar ethene, 30 °C, 15 μmol Ti, Al:Ti = 1000, 30 min run time).

Catalyst (R)	C_6 products [g] (wt %)	C_{10} products [g] (wt %)	PE [g] (wt %)	Productivity[a]
1 (Ph)	20.9 (83)	3.5 (14)	0.5 (1.8)	2787
2 (3,5-$Me_2C_6H_3$)	7.9 (93)	0.5 (5)	0.1 (1.3)	1053
3 (Me)	0.5 (17)	0.1 (4)	2.4 (76)	66

[a] In kg C_6 product per mole Ti and h.

whereas the absence of a pendant arene group leads to the predominant formation of PE. This indicates that a) the pendant arene group is essential to obtaining selective trimerization, and that b) this catalysis is likely to involve reversible coordination of the arene moiety to the metal center. It may be noted that even for the *tert*-butylcyclopentadienyl system **3**/MAO some ethene trimerization is observed. A related observation was made recently by Pellecchia et al. in ethene polymerization with $[(\eta^5\text{-}C_5Me_5)TiMe_2]\text{-}[MeB(C_6F_5)_3]$ in toluene as catalyst, where the PE obtained contains a noticeable amount of *n*-butyl side groups.[5] It was suggested that the catalyst is partly converted to a species that trimerizes ethene to 1-hexene, which is then incorporated into the polymer. Our observations indicate that transient coordination of the toluene solvent to the metal center may be instrumental in this,[6] albeit less efficient than the pendant arene group in the $[(\eta^5\text{-}C_5H_4CMe_2Ar)TiCl_3]$/MAO systems as the interaction is intermolecular rather than intramolecular.

The only family of catalysts known thus far to give highly selective ethene trimerization is based on chromium (mixtures of Cr salts with alkylaluminum compounds and added ligands, especially imidazoles, or coordinating solvents such as 1,2-dimethoxyethane).[7] Very recently, selective trimerization of higher alkenes with triazacyclohexane – chromium species was also reported.[8] The catalysis in these systems is proposed to proceed via metallacyclic intermediates, chromacyclopentanes and chromacycloheptanes, where β-H abstraction from the latter, followed by reductive elimination, leads to 1-hexene formation and a low-valent Cr species. The latter can then couple two ethene molecules to regenerate the chromacyclopentane.[9, 10] It is possible that a similar cycle is operative in the present titanium system. Several catalytic C-C coupling reactions have been reported in neutral Ti systems that involve the Ti^{IV}/Ti^{II} couple (e.g., in the bis-(aryloxy)titanium compounds).[11] The question is then how the system converts from the cationic species $[(C_5H_4CMe_2Ar)TiMe_2]^+$ (generated by the reaction of the corresponding trichloride with MAO) to a cationic metallacyclopentane. A proposal for this process is shown in Scheme 1.

The initially generated species $[(C_5H_4CMe_2Ph)TiMe_2]^+$ will undergo multiple ethene insertions into the Ti−Me bonds (where during ethene capture the arene is likely to be noncoordinating) to produce bis(*n*-alkyl) compounds $[(C_5H_4CMe_2Ph)Ti(CH_2CH_2R)_2]^+$. These are in equilibrium (through β-H elimination) with hydride – olefin species. Normally, dissociation of the olefin is energetically unfavorable unless it is driven out by another incoming ligand (e.g.,
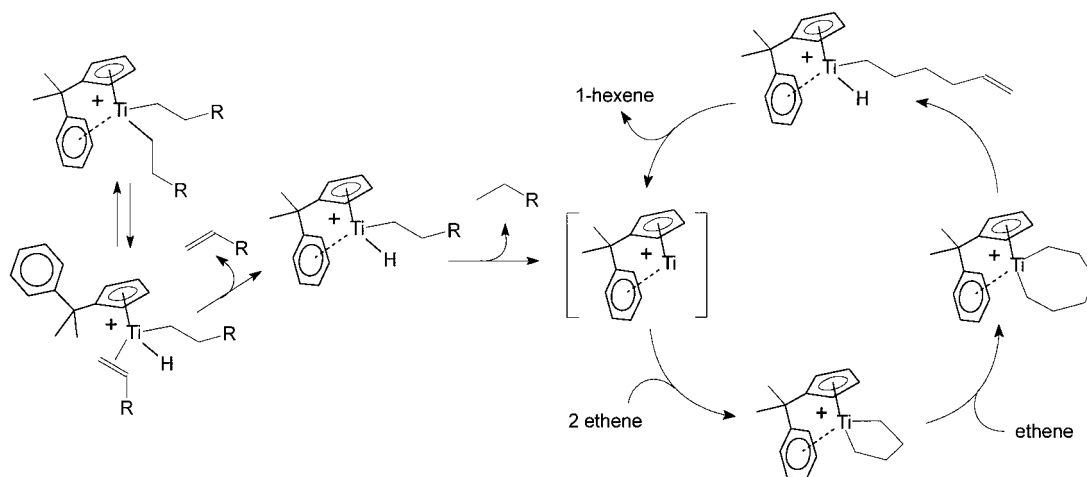
Scheme 1. Proposed reaction pathway for catalyst transformation and catalytic ethene trimerization in the system studied.

ethene, which will then rapidly insert into the M—H bond, resulting in the normal chain transfer process for catalytic ethene polymerization).[12] In the system with the pendant arene group it is possible that the alkene is driven out by the incoming arene, which will lead to a 16-electron hydride–alkyl species, $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ph)Ti(H)(CH_2CH_2R)]^+$. Reductive elimination then releases CH_3CH_2R and forms a Ti^{II} intermediate which can capture two ethene molecules to give a cationic titanacyclopentane. This species can then perform the catalytic ethene trimerization (Scheme 1), following the pathway described above for the Cr-based catalysts.

We are presently investigating the validity of this proposal. Although we did observe that the independently generated ionic species $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ar)TiMe_2][MeB(C_6F_5)_3]$ reacts with ethene in $[D_8]$toluene to generate 1-hexene (NMR tube experiment), we have as yet not been successful in observing and isolating the proposed cationic titanacyclopentane intermediate. Nevertheless, we feel that the present proposal is reasonable given the observations made thus far.

In conclusion, we have identified a catalyst system, $[(\eta^5\text{-}C_5H_4CMe_2R)TiCl_3]$/MAO, that, by attachment of a pendant arene group to the cyclopentadienyl ancillary ligand (R = aryl), can be transformed from an ethene polymerization catalyst to a selective ethene trimerization catalyst. Although ethene oligomerizations that produce 1-hexene in excess of the amount expected from Schultz–Flory product distributions, and ethene polymerization catalysts that produce branched polyethenes are known (e.g., for certain Ziegler-type catalyst systems),[13] to our knowledge the present system is the first highly selective ethene trimerization catalyst that is not based on chromium. The principle that a hemilabile ligand functionality can divert the metal species from one catalytic cycle into another may be applicable to other types of catalysis.

Experimental Section

All manipulations of catalyst and cocatalyst solutions were carried out under purified nitrogen atmosphere using standard glove-box and Schlenk techniques. The compounds **1–3** were prepared according to literature procedures.[3, 4] A toluene solution of MAO (26 wt%, Akzo Nobel Chemicals) was used as received. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3–11 supported Cu oxygen scavenger, and molecular sieves (4 Å) under nitrogen atmosphere prior to use. Ethene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (4 Å). Cyclooctane (used as internal standard) was distilled from sodium prior to use. Product analyses were performed by GC on a HP 6890 instrument equipped with a HP-1 dimethylpolysiloxane column (19095 Z-123) and by GC/MS using a HP 5973 mass-selective detector attached to a HP 6890 GC instrument.

General procedure for the catalytic ethene conversions: A stainless-steel 1-L autoclave (Medimex), fully temperature- and pressure-controlled and equipped with solvent and catalyst injection systems, was preheated in vacuo for 45 min at 100 °C. The reactor was cooled to the desired temperature, charged with 200 mL of toluene, and pressurized with ethene. After equilibrating for 15 min, the appropriate amount of MAO/toluene was injected, together with 25 mL of toluene. Subsequently, a mixture of 2.50 mL of cyclooctane (internal standard) and 1.0 mL of a 15 mM stock solution of the titanium halide complex in toluene was injected, together with 25 mL of toluene, to start the reaction. During the reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. The run was ended by adding an aliquot of ethanol, and the reactor was vented. Remaining residual MAO was destroyed by adding further ethanol, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The polymer was stirred for 1 h in acidified ethanol, repeatedly rinsed with ethanol on a glass frit, and dried in vacuo at 70 °C overnight.

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An Insoluble Polymer-Bound Bis-Oxazoline Copper(II) Complex: A Highly Efficient Heterogeneous Catalyst for the Enantioselective Mukaiyama Aldol Reaction**

Simonetta Orlandi, Alessandro Mandoli, Dario Pini, and Piero Salvadori*

In recent years asymmetric catalytic procedures have been emerging as a major option for the preparation of chiral compounds in enantiomerically enriched form, especially when the catalyst system consists of readily available, cheap and nontoxic components.[1] However, the recovery of the catalyst and its reuse is often mandatory for large-scale applications. At present, one of the most promising solutions for this problem seems to be the anchoring of effective soluble systems on an insoluble matrix, ideally without any reduction of catalytic performances with respect to the homogeneous phase.[2, 3] While this strategy is well established in reduction and oxidation processes,[4, 5] few examples have been reported for C–C bond-forming reactions.[6]

In our continuing effort to develop heterogeneously catalyzed asymmetric Mukaiyama aldol reactions,[7] we became interested in bis-oxazoline (box) ligands 1.[8] In spite of the versatility of this class of chiral auxiliaries, few supported copper box complexes have been reported to date.[9] They rely on ion exchange to anchor them to an organic or inorganic host. The application of these


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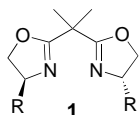
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immobilized catalysts to asymmetric cyclopropanation and aziridination led to modest enantioselectivity, which could be related to unfavorable interactions between the metal complex and the support.[10, 11] Better results were recently reported by Evans et al. for a hetero Diels–Alder reaction with Cu^{II}–box in the presence of Florisil, although the use of a poor solvent for the metal complex was required for effective recovery of the catalyst.[12]

To develop a versatile, reusable, insoluble box ligand equivalent to the homogeneous systems **1**, the preparation of bis-oxazoline covalently bound to an inert polystyrene matrix was designed. The chiral monomer **2a** was synthesized by the route depicted in Scheme 1,[13] together with the soluble model **2b** of the supported ligand.

2a Ar = 4-CH$_2$CHC$_6$H$_4$
2b Ar = Ph
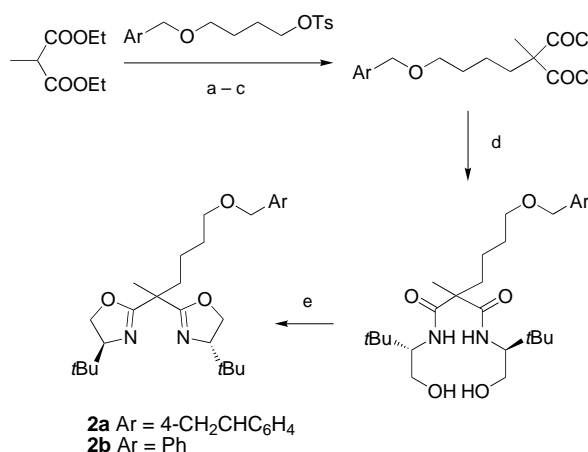
Scheme 1. a) NaH, THF, reflux, 24 h, 65–95%; b) 18 M KOH, reflux, 3 h, 82–89%; c) (COCl)$_2$, cat. DMF, CH$_2$Cl$_2$, RT, 18 h; d) (*S*)-*t*BuCH(NH$_2$)-CH$_2$OH (2 equiv), Et$_3$N, CH$_2$Cl$_2$, RT, 35 min; e) TsCl, Et$_3$N, cat. DMAP, CH$_2$Cl$_2$, RT, 27 h, 50–55% over two steps. Ts = *p*-toluenesulfonyl, DMAP = 4-dimethylaminopyridine.

The AIBN-initiated copolymerization of **2a** with styrene and divinylbenzene (DVB), in the presence of toluene as a porogen agent,[14] followed by exhaustive extraction with THF and CH$_2$Cl$_2$, afforded **3** (Scheme 2). It was characterized by IR spectroscopy ($\tilde{\nu}_{C=N} = 1655$ cm^{-1}),[15] and its content of chiral ligand (0.31 mmol g^{-1}) was evaluated by nitrogen elemental analysis. A maximum metal uptake of 0.18 mmol g^{-1} was determined by equilibrating **3** with an excess of Cu(OTf)$_2$ in THF.

3
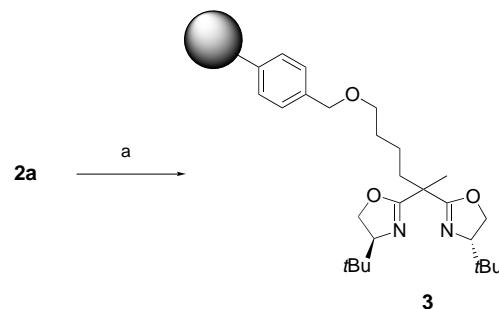
Scheme 2. a) Styrene, DVB (**2a**:styrene:DVB = 7:42:51), AIBN, toluene (60% v/v), 80°C, 18 h. AIBN = azobisisobutyronitrile.