New Tantalum Ligand-Free Catalyst System for Highly Selective Trimerization of Ethylene Affording 1-Hexene: New Evidence of a Metallacycle Mechanism

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Linear α-olefins (LAOs) are important industrial chemicals produced by metal-catalyzed oligomerization of ethylene. Even when using sophisticated catalyst systems to generate LAOs, however, the formation of α-olefin mixtures is unavoidable, due to a Shultz−Flory distribution.[1] The initial discovery of the chromium-based selective ethylene trimerization giving 1-hexene[2] prompted both academic and industrial groups to develop several highly selective and productive ethylene trimerization[3] and tetramerization[4] catalyst systems, affording 1-hexene and 1-octene, respectively, which are comonomers that are in high demand for linear low density polyethylene production. Mainly titanium- and chromium-based catalysts have been designed by tuning the stabilizing ligands, the oxidation state of the catalytic active centers, and the choice of the cocatalyst. To achieve catalytic activity among the wide variety of catalyst systems developed to date, there is an essential requirement for conventional cocatalysts, such as a large excess of aluminum compounds or perfluoro borane derivates. As a parallel approach with the same importance, considerable efforts[5] over the past two decades have been applied to clarify the metallacycle mechanism, which was originally proposed to be the mechanism most likely responsible for the selective trimerization of ethylene.[2b] The restrictions of the reported catalytic systems, however, due to the nature of paramagnetic metal centers and/or the presence of cocatalysts, have hampered the ability to obtain direct evidence. Sen et al. reported that Ta(III) species derived from the reaction of TaCl₅ and alkylating reagents such as ZnMe₂ became active catalysts for ethylene trimerization.[3m] Herein, we report a new methodology to generate ligand-free Ta(III) species capable of catalyzing the trimerization of ethylene to 1-hexene with >98% selectivity without any detection of internal olefins. Moreover, new evidence to support the metallacycle mechanism has been reported.

Our new catalytic system consists of the salt-free reduction of TaCl₅ with 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (BTCD) or its methyl derivative (MBTCD) in the presence of ethylene, producing 2 equiv of Me₃SiCl, C₆H₅R, and Ta(III) species active for ethylene trimerization. The trimerization reactions of ethylene were performed in a stainless steel autoclave at 70 and 100 °C, using variable ethylene pressure. Representative results are shown in Table 1.[6] Catalytic activity (up to 1008 TOF per [Ta]·h) was significantly higher than that reported for the TaCl₅/ZnMe₂ system.[3m] Selectivity for 1-hexene among oligomers was very high, reaching up to 98.5% with only a trace amount of polyethylene as the byproduct. Slightly excess amounts of reducing agents resulted in the best catalytic activity for the trimerization, corresponding to the complete conversion of TaCl₅ to TaCl₃.[6] When hexamethylbenzene (HMB) was added to this system, no trimerization

Table 1. Trimerization of C₂H₄ by TaCl₅/MBCTD System[a]

entry	C₂H₄ (atm)	temp (°C)	time (h)	TOF[b]	1-hexene selectivity (%)[c]	PE (%)[c]
1	48	70	1	979	98.5	0.7
2	25	70	1	845	97.9	0.9
3	6	70	1	238	95.1	2.6
4	48	100	4	1008	95.8	1.1
5[d]	48	100	4	981	98.0	0.2

[a] Reaction conditions: 0.2 mmol of TaCl₅, 0.45 mmol of MBTCD, 200 mL of toluene, 400 mL of stainless steel autoclave. [b] For 1-hexene, expressed in mmol of 1-hexene/mmol of TaCl₅·time (h). [c] Relative to all soluble oligomers and polyethylene. [d] *o*-Dichlorobenzene (200 mL) was used as solvent.

Scheme 1
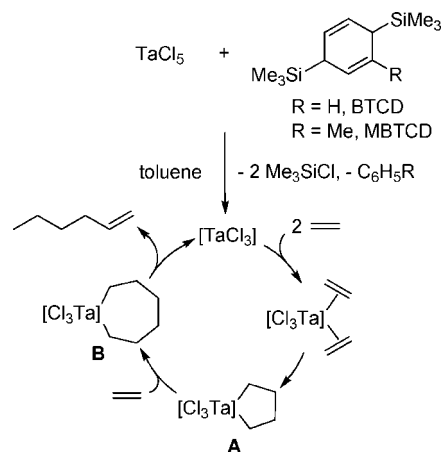
proceeded, indicating aromatic groups might interact and stabilize the highly unsaturated Ta(III) species.[7]

Our catalyst system possesses some advantages: (1) a high solubility of catalytic active species in aromatic solvents, e.g., toluene, keeping this system homogeneous; (2) no requirement for conventional cocatalysts such as alkylaluminum and borane compounds; (3) the ability to undergo trimerization of ethylene at low ethylene pressure (6 atm).

As shown in Scheme 1, two molecules of ethylene concertedly coordinate to an *in situ* generated Ta(III) active species, yielding a tantalacyclopentane intermediate **A**. As demonstrated by the theoretical calculation of Houk et al.,[8] the insertion of the third ethylene molecule to **A** produces a more unstable and flexible tantalacycloheptane intermediate **B**,[9] which readily results in the selective formation of 1-hexene and the subsequent regeneration of tantalum(III) species.

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Scheme 2
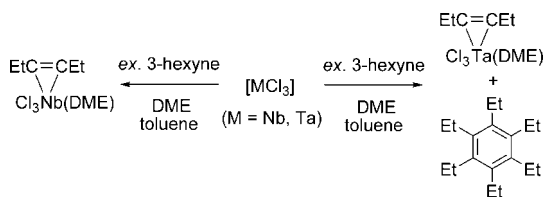
On measuring Variable Temperature (VT) NMR spectroscopy, the expected metastable tantalacyclopentane intermediate **A**, a key intermediate of the metallacycle mechanism (Scheme 1), was detected. When the *in situ* reduction of TaCl₅ with BTCD in the presence of ethylene (2 atm) was conducted at −10 °C, we observed the catalytic formation of 1-hexene and small peaks, two broad multiplets at 2.55 and 1.74 ppm, which were assigned to the sp^3 α and β-methylene protons, respectively, of the tantalacyclopentane **A**, whose chemical shift values were comparable to those previously reported for some tantalacyclopentane complexes (2.22−2.89 for α-H, and 0.96−1.68 for β-H).[10] Based on the intensity of the methylene protons with respect to the intensity of Me₃SiCl, 2% of reduced tantalum species was converted to the metallacycle intermediate. Clear correlation between these two signals was demonstrated by $^1H-^1H$ COSY at low temperature, but no other correlation was observed.[6] When the solution was warmed to 20 °C, both multiplet signals disappeared and the amount of 1-hexene increased. Additionally, the existence of tantalacyclopentane **A** was confirmed by a quenching experiment: addition of bromine solution in CH₂Cl₂ gave the expected 1,4-dibromobutane.[6] There is other clear evidence for Ta(III) that some Ta(III)-alkyne complexes could be formed,[11] though accompanied with catalytic alkyne trimerization (Scheme 2).[6]

Our new methodology is also efficient for generating low-valent niobium species, *i.e.*, Nb(III), which has been reported and *in situ* generated by treating NbCl₅ with 2 equiv of Bu₃SnH in the presence of 3-hexyne.[12] Reduction of NbCl₅ with BTCD in the presence of 3-hexyne induced the formation of a 3-hexyne complex, NbCl₃-(3-hexyne)(DME),[6] but we observed no catalytic activity for trimerization of 3-hexyne (Scheme 2).[13]

In summary, we developed a new methodology for generating Ta(III) species as a highly active catalyst for the selective trimerization of ethylene, giving 1-hexene under mild conditions (even at low temperature and low pressure). We also provide evidence that tantalacyclopentane is involved in the metallacycle mechanism underlying the selective oligomerization of ethylene. In contrast to other known trimerization catalyst systems where supporting ligands have an important role in the selective trimerization of ethylene, our system is unique in that it requires no organic supporting ligands or salt contact, only halogen ligands. The generation of low-valent metal species without the formation of any salts is part of our ongoing research.

Supporting Information Available: Experimental procedures, selected 1D and 2D NMR spectra (PDF). CIF file giving data for NbCl₃(3-hexyne)(DME) complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA8100837