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Communications to the Editor

New Tantalum-Based Catalyst System for the Selective Trimerization of Ethene to 1-Hexene

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The catalytic oligomerization of ethene typically leads to a broad Schultz−Flory distribution of 1-alkenes and specific 1-alkenes are obtained by fractional distillation of the mixture.[1] However, only some of these are commercially useful. The most important is 1-hexene, which is required for the synthesis of linear low-density polyethene (LLDPE).[2] In principle, a catalytic system that trimerizes ethene specifically to 1-hexene would be much more useful from a practical standpoint. The only known ethene trimerization systems are all based on chromium compounds possessing nitrogen or oxygen ligands.[3] Herein, we describe a simple, "ligand-less", tantalum-based system for the selective trimerization of ethene to 1-hexene. A rate in excess of 500 mol of ethene consumed/mol of Ta•h with 96−99% selectivity for 1-hexene has been observed.

The system consists of two components: tantalum(V) chloride and an alkylating agent. The reactions were typically carried out in chlorobenzene in a glass-lined autoclave at 45−60 °C, using an ethene pressure of 700 psi. NMR spectroscopy indicated the complete absence of internal alkenes in the product mixture. The ethene oligomers were further analyzed and quantified by gas chromatography. Besides 1-hexene, other oligomers detected by GC (and verified by GC-MS) were even numbered 1-alkenes, such as butene, octene, and decene. Our results are summarized in Table 1.

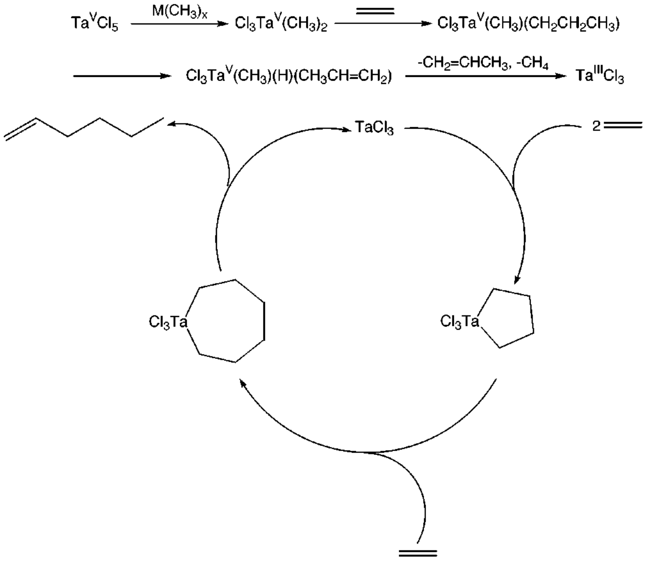
The alkylating agents employed can be divided into two groups, the second of which are the lithium reagents. Among the nonlithium-based alkylating agents, only those that are methylating agents appear to work well. When other alkyl or aryl groups were employed, the activity was sharply attenuated and the formation of polyethene was sometimes observed. With lithium reagents, higher alkyls or phenyl were also effective although the overall activity was lower than that observed with $Sn(CH_3)_4$ or $Zn(CH_3)_2$. Note that the activity reported for CH_3Li is deceptive, given the low solubility of the reagent in the reaction mixture.

Table 1. Catalytic Trimerization of Ethene[a]

entry	alkylating agent (equiv)	temp (°C)	polyethene (g)	1-hexene selectivity (mol %)[b]	activity (turnovers/ Ta•h)[c]
1	$Sn(CH_3)_4$ (2)	45	trace	94	385
2	$Sn(CH_2CH_3)_4$ (2)	45	trace	98	40
3	$SnPh_4$ (1)	45	0.43	26	5
4[d]	$Zn(CH_3)_2$ (1)	45	trace	96	460
5	$Al(CH_3)_3$ (0.66)	45	trace	94	230
6[d]	CH_3Li (2)	60	0.10	91	90
7[e]	$CH_3(CH_2)_3Li$ (1)	60	trace	95	20
8[f]	$CH_3(CH_2)_3Li$ (2)	60	trace	99	195
9	$(CH_3)_3CLi$ (1.5)	60	trace	98	135
10	PhLi (2)	60	trace	99	185

[a] Reaction conditions: 0.050 mmol $TaCl_5$, 10 mL of chlorobenzene, 4 h, 125 mL glass-lined stainless steel autoclave, 700 psi ethene. [b] Relative to all soluble oligomers (1-alkenes). [c] For 1-hexene. [d] 0.50 mmol $TaCl_5$. [e] 0.14 mmol $TaCl_5$. [f] 0.10 mmol $TaCl_5$.

Scheme 1



Our working mechanism for the selective trimerization of ethene is shown in Scheme 1. A tantalum(III) species is generated initially and reacts with two ethene molecules to form a tantalum(V) metallacyclopentane, which Schrock has shown to be a facile reaction.[4] A third molecule of ethene inserts to form a metallacycloheptane. β-Hydrogen abstraction from this species leads to the formation of a tantalum(V) alkylhydride. Reductive elimination regenerates tantalum(III) and 1-hexene. The observed selectivity suggests that β-hydrogen abstraction is much more facile from the larger, more flexible, seven-membered ring compared to the metallacyclopentane.[5]

How is the initial tantalum(III) species formed? The sodium amalgam reduction of $TaCl_5$ in the presence of ethene did not

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lead to catalytic trimerization, perhaps due to overreduction. However, as discussed below, we believe that the reaction of the alkylating agent with $TaCl_5$ results in the formation of TaR_2Cl_3, which yields tantalum(III) upon reaction with ethene.

It is known that the addition of an alkylating agent in various ratios to $TaCl_5$ will form the mono-, di-, and tri-alkylated species in solution.[6] The reaction of 0.25 equiv of $Zn(CH_3)_2$ to $TaCl_5$ in chlorobenzene resulted in the formation of $Ta(CH_3)Cl_4$ (^1H NMR: 2.04 ppm). Similarly, the addition of 1 equiv of $Sn(CH_3)_4$ caused the formation of a mixture of $Ta(CH_3)Cl_4$ and $Ta(CH_3)_2Cl_3$ (^1H NMR: 1.65 ppm). Further addition of $Zn(CH_3)_2$, $Sn(CH_3)_4$, or CH_3Li resulted in the formation of a mixture of $Ta(CH_3)_2Cl_3$ and $Ta(CH_3)_3Cl_2$ (^1H NMR: 1.49 ppm). The catalytic formation of 1-hexene from ethene was found to occur ***only*** when $Ta(CH_3)_2Cl_3$ was present in solution suggesting that the dimethyl tantalum(V) compound was the immediate precursor to the active catalyst. Information concerning the reduction of this compound to the active catalyst was obtained by monitoring the reaction of $TaCl_5$ with CD_3Li and ethene by ^2H NMR spectroscopy in chlorobenzene. Upon mixing of $TaCl_5$ and CD_3Li, the formation of the di- and trimethyl tantalum(V) compounds was observed. The subsequent addition of ethene (200 psi) resulted in the formation of 1-hexene. At the same time, ^2H NMR spectroscopy revealed the formation of CD_3H (0.1 ppm, doublet) and a terminal CD_3 group (0.8 ppm, multiplet). No other prominent ^2H NMR resonance was observed over the course of 20+ hours. The above set of observations can be rationalized by the mechanism shown at the top of Scheme 1. The sequence of steps involves (a) insertion of ethene into one of the Ta−methyl bonds of the dimethyl tantalum(V) species, (b) β-hydrogen abstraction to form a tantalum(V) methylhydride and propene, and (c) reductive elimination to (propene-coordinated) $TaCl_3$ and methane. The propene formed apparently enters the oligomerization cycle. This is supported by the observation of odd-carbon α-alkenes when a mixture of 700 psi ethene and 7 g of propene was used as the feed for the catalyst system. Finally, 1 equiv of benzene was formed when the combination of $TaCl_5$ + PhLi was used to trimerize ethene, suggesting a similar mechanism for the formation of the active species from $TaPh_2Cl_3$.

The final confirmation of the intermediacy of $Ta(CH_3)_2Cl_3$ was obtained in the following way. An approximately 1:2 mixture of $Ta(CH_3)Cl_4$ and $Ta(CH_3)_2Cl_3$ was prepared by the reaction of $TaCl_5$ with $Zn(CH_3)_2$. This mixture was purified to remove the starting materials including the alkylating agent, and the ratio of $Ta(CH_3)Cl_4$ to $Ta(CH_3)_2Cl_3$ was determined by ^1H NMR to be 35 to 65. Upon exposing the mixture to ethene under the reaction conditions, the formation of 1-hexene occurred at a rate calculated to be 540 turnovers/$Ta(CH_3)_2Cl_3$•h. As anticipated, this rate significantly exceeds those shown in Table 1 since $Ta(CH_3)_2Cl_3$ is not formed quantitatively by simply adding the methylating agent to $TaCl_5$. ^1H NMR studies, carried out using 200 psi of ethene and mixtures of $Ta(CH_3)_3Cl_2$ and $Ta(CH_3)_2Cl_3$, revealed that the concentration of $Ta(CH_3)_2Cl_3$ decreased relative to $Ta(CH_3)_3Cl_2$ as the reaction progressed. On the other hand, a solution of only $Ta(CH_3)_3Cl_2$ was not active for ethene trimerization. The above evidence, taken together, strongly suggests that *$Ta(CH_3)_2Cl_3$ is the single-site precursor to the active catalyst.*

In conclusion, a new, “ligand-free”, catalyst system for the selective trimerization of ethene to 1-hexene has been discovered. A rate in excess of 500 mol of ethene consumed/mol of Ta•h with 96−99% selectivity for 1-hexene has been observed. We are currently examining the detailed mechanism of the ethene trimerization step.

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