

Article

# Selective Trimerization of $\alpha$ -Olefins with Immobilized Chromium Catalyst for Lubricant Base Oils

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**Abstract:** The demand for poly( $\alpha$ -olefin)s (PAOs), which are high-performance group IV lubricant base oils, is increasingly high. PAOs are generally produced via the cationic oligomerization of 1-decene, wherein skeleton rearrangement inevitably occurs in the products. Hence, a transition-metal-based catalytic process that avoids rearrangement would be a valuable alternative for cationic oligomerization. In particular, transition-metal-catalyzed selective trimerization of  $\alpha$ -olefins has the potential for success. In this study, (*N,N',N''*-tridodecyltriazacyclohexane)CrCl<sub>3</sub> complex was reacted with MAO-silica (MAO, methylaluminoxane) for the preparation of a supported catalyst, which exhibited superior performance in selective  $\alpha$ -olefin trimerization compared to that of the corresponding homogeneous catalyst, enabling the preparation of  $\alpha$ -olefin trimers at ~200 g scale. Following hydrogenation, the prepared 1-decene trimer (C<sub>30</sub>H<sub>62</sub>) exhibited better lubricant properties than those of commercial-grade PAO-4 (kinematic viscosity at 40 °C, 15.1 vs. 17.4 cSt; kinematic viscosity at 100 °C, 3.9 vs. 3.9 cSt; viscosity index, 161 vs. 123). Moreover, it was shown that 1-octene/1-dodecene mixed co-trimmers (i.e., a mixture of C<sub>24</sub>H<sub>50</sub>, C<sub>28</sub>H<sub>58</sub>, C<sub>32</sub>H<sub>66</sub>, and C<sub>36</sub>H<sub>74</sub>), generated by the selective supported Cr catalyst, exhibited outstanding lubricant properties analogous to those observed for the 1-decene trimer (C<sub>30</sub>H<sub>62</sub>).

**Keywords:** selective  $\alpha$ -olefin trimerization; lubricant base oil; supported catalyst; chromium

## 1. Introduction

The materials obtained by oligomerization of linear  $\alpha$ -olefins (LAOs, i.e., 1-alkenes) are referred to as poly( $\alpha$ -olefin)s (PAOs) and they are extensively utilized as high-performance group IV lubricant base oils [1–7]. PAOs are routinely produced via the oligomerization of 1-decene using cationic initiators (e.g., BF<sub>3</sub>-ROH), followed by a hydrogenation process [8–12]. These PAOs display outstanding lubricant properties, relative to those of Group I through III base oils, such as excellent viscosity indices, low pour points, and high oxidative stabilities. In the cationic oligomerization of 1-decene, a wide range of n-mers (i.e., dimer, trimer, tetramer, pentamer, etc.) are generated. The trimer is the major product of the cationic oligomerization process, and is fractionated by distillation; the trimer fraction containing a small amount of tetramer and pentamer is referred to as PAO-4, and is used in many industrial and automotive lubricant applications such as gear oils, compressor oils, engine oils, hydraulic fluids, and greases.

In the cationic oligomerization of 1-decene, carbocation rearrangement is concomitant, leading to severe skeleton rearrangement, as well as the formation of tetra-substituted olefins, which are resistant

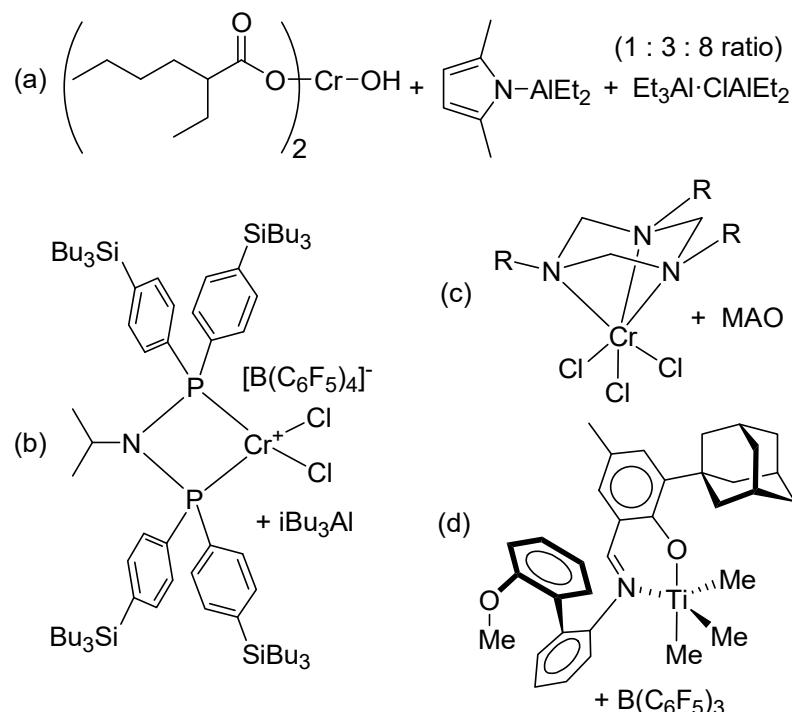
to hydrogenation [13,14]. In particular, numerous methyl groups are generated at random positions along the carbon chain, leading to deterioration in lubricant properties. PAOs can also be prepared using transition-metal-based catalysts (e.g., metallocene catalysts), whereby n-mers are generated via sequential 1,2-insertion and  $\beta$ -elimination processes [15–20]. Thus, skeleton rearrangement, occurring in cationic oligomerizations, can be avoided. A portion of PAOs are currently produced via metallocene catalysis of 1-decene [21,22]. However, in this case, a wide range of n-mers require fractionation via an energy-intensive distillation process. Catalysts which are selective for trimers have also been discovered, however, their performance is inadequate for commercialization, their turnover number (TON) is low (<6000), and they necessitate low-temperature conditions (<20 °C) [23–27]. Moreover, lubricant properties evaluated for 1-decene trimer samples prepared on a laboratory scale were reportedly not superior to those of PAO-4 fractionated in the cationic oligomerization process, and while their lubricant properties were inferior to those of the product fractionated in the metallocene oligomerization process, the two carbon skeletons were comparable [1,24].

While the demand for PAOs is increasingly high, their market expansion is curtailed by the limited supply of 1-decene. 1-Decene is produced via oligomerization of ethylene, whereby, in addition to the formation of 1-decene, a wide range of LAOs (Schulz-Flory distribution) are generated [28]. Each  $\alpha$ -olefin is fractionated by distillation for appropriate applications. 1-Butene, 1-hexene, and 1-octene are used as co-monomers in the polyolefin industry; 1-decene is used mainly for the production of PAOs; 1-dodecene, 1-tetradecene, and 1-hexadecene are functionalized for detergents; 1-tetradecene, 1-hexadecene, and 1-octadecene are isomerized into biodegradable offshore drilling fluids; 1-octadecene and heavier LAOs (C20–24) are used as lubricant oil additives and functional fluids. With outstanding lubricant properties, PAOs produced from 1-decene are sold at a high price, while other  $\alpha$ -olefin oligomers (e.g., 1-octene oligomers and 1-dodecene oligomers) exhibit inferior properties as lubricant base oils. It is important to consider whether a courier selectively generated from a mixed 1-octene/1-dodecene feed would exhibit lubricating properties comparable to those of PAOs prepared solely from 1-decene. 1-Dodecene and 1-octene may not be restricted by a limited supply–demand predicament, unlike 1-decene. In the early 2000s, a catalytic system for the selective generation of 1-octene was discovered [29–32]. Recently, we also discovered a highly efficient and economical catalytic system for 1-octene production [33–35]. It is anticipated that, in the near future, 1-octene will be produced cleanly, without the generation of a wide range of other LAOs in the process.

## 2. Results and Discussion

### 2.1. Catalyst Screening

As the titanium-based selective ethylene trimerization catalyst is known to be active for  $\alpha$ -olefin trimer production (Figure 1d) [36–38], chromium-based catalysts that are highly active for ethylene trimerization or tetramerization were screened. Phillips Catalyst (Figure 1a), which is commercially used for 1-hexene production, did not display any activity for  $\alpha$ -olefin production [39]. An MAO-free catalytic system for ethylene tetramerization (Figure 1b) exhibited a reasonably high activity with 1-octene [33]. At an optimized reaction temperature of 90 °C and after 16 h of operation, a high turnover number (TON) of 17,500 was attained with a high conversion of 1-octene (60%) (see SI for details). However, product analysis by GC indicated that trimers were not selectively generated. Instead, dimers (82%) were predominantly generated, along with a minor number of trimers (18%). A chromium-based catalytic system (Figure 1c) that can selectively generate  $\alpha$ -olefin trimers was discovered two decades ago [23]. However, the triazacyclohexane chromium catalyst activated with methylaluminoxane (MAO) could be readily deactivated even at room temperature and the attained TON was limited to below 1000 by the need to perform the reaction at 0 °C for 20 h in toluene (*v/v*, 1:1) [24]. Selectivity for the trimer was not complete, being in the range of 80–93%. Later, a higher TON of up to 5000 was realized with improved trimer selectivity (>99%), by performing the reaction in *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> solvent with a triazacyclohexane chromium complex bearing a -CH<sub>2</sub>CH<sub>2</sub>CH[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> fragment.



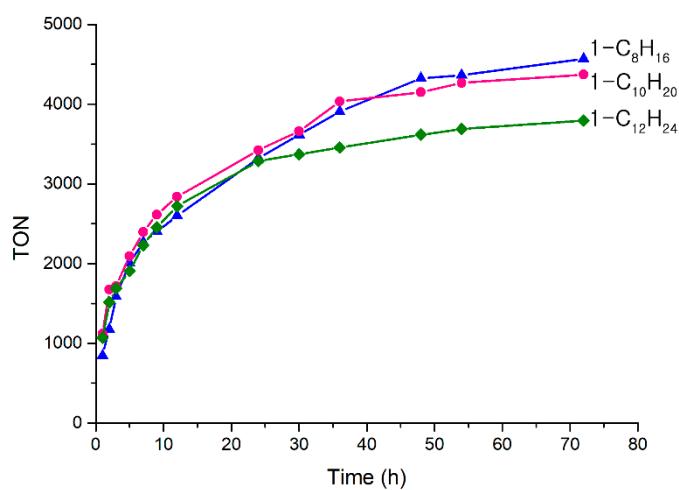
**Figure 1.** Ethylene or  $\alpha$ -olefin trimerization (or tetramerization) catalysts (a): Phillips ethylene trimerization catalyst; (b): MAO-free ethylene tetramerization catalyst; (c) and (d): selective  $\alpha$ -olefin trimerization catalyst.

In the case of titanium-based catalysts (Figure 1d), it was demonstrated that their catalytic performance could be improved by anchoring the activated catalyst on silica; that is, the supported catalyst, prepared by reacting the appropriate titanium complex with MAO attached to silica (MAO-silica), exhibited superior longevity, and thus a 10-fold higher TON of up to 6000 [26,40]. Prior to their publication, we likewise noted that the supported catalyst, prepared by reaction of a triazacyclohexane chromium complex with MAO-silica, exhibited enhanced performance compared to that of the homogeneous version of the catalyst [41].

## 2.2. $\alpha$ -Olefin Oligomerization Studies with Supported Catalysts

In this study, we investigated the performance of a supported catalyst, prepared by reacting a triazacyclohexane chromium complex with MAO-silica. MAO-silica was prepared by reacting MAO and silica (pore volume,  $1.6 \text{ cm}^3/\text{g}$ ; surface area,  $309 \text{ m}^2/\text{g}$ ; mean particle size,  $30 \mu\text{m}$ ), which are both commonly used in the polyolefin industry [42]. When MAO and silica were reacted in 1: 2 weight ratio, the majority (~95%) of MAO had bonded with silica to achieve optimal MAO coverage (5.6 mmol-Al/g). The supported catalyst was prepared by reacting  $(N,N',N''\text{-tridodecyltriazacyclohexane})\text{CrCl}_3$  ( $R = \text{dodecyl}$  in Figure 1c;  $[(C_{12}\text{H}_{25})_3\text{TAC}]\text{CrCl}_3$ ) with the prepared MAO-silica in toluene. The  $[(C_{12}\text{H}_{25})_3\text{TAC}]\text{CrCl}_3$  content was varied at 25, 50, and 75 mg, while the amount of MAO-silica was fixed at 1.0 g ( $\text{Al/Cr} = 170, 84, 56$ ). It was evident that all the fed chromium complexes were anchored on the silica surface in all cases, as the toluene phase of the filtrate was colorless after the reaction, while the toluene solution of  $[(C_{12}\text{H}_{25})_3\text{TAC}]\text{CrCl}_3$  was purple. The fabricated supported catalysts (100 mg) were suspended in neat 1-octene (5.0 g) at room temperature for 24 h to determine the optimum loading of the chromium complex. With a chromium complex loading of 25 mg, 21% of 1-octene was converted to trimer. By increasing the loading amount of chromium complex to 50 mg, the conversion increased to 30%. However, increasing the loading further to 75 mg did not improve the conversion beyond 30%.

To investigate the effect of temperature on catalyst performance, conversions were monitored over time using optimized supported catalyst parameters (50 mg Cr complex/1.0 g MAO-silica; Al/Cr = 84), at temperatures of ~25 (rt), 40, 60, and 80 °C, under the same catalyst feed (400 mg, 25 µmol Cr) in 20 g of neat 1-octene (Table S1). Plots of conversion vs. reaction time clearly indicated that the reaction rate increased with an increase in temperature up to 60 °C, and conversions attained at 72 h were 44%, 59%, and 64% at ~25, 40, and 60 °C, which corresponded to TONs of 3100, 4200, and 4600, respectively (Figure 2). Increasing the temperature from 60 to 80 °C led to deterioration in the conversion rate, likely attributed to severe deactivation of the catalyst at high temperature. At temperatures of ~25, 40, and 60 °C, the conversion did not linearly increase with reaction time, but reached a plateau following rapid growth in the early stages of the reaction, which indicated that catalyst deactivation was inevitable even at low temperatures, although the deactivation process was curbed by lowering the temperature. When the oligomerization was performed under identical conditions of 60 °C, with the same amount of chromium complex and MAO (Cr = 25 µmol; Al/Cr = 100), but in the homogenous phase, 31% conversion was achieved in a relatively short time of 3 h; however the conversion could not be improved further by extending the reaction time, indicating that the catalyst was completely deactivated within 3 h. In the homogeneous phase, some bimolecular deactivation process is proposed to occur, which might be retarded by immobilization, resulting in an increase in productivity with the prolonged catalyst lifetime. Deactivation process might not be related to the action of residual trialkylaluminum in MAO, because the addition of Et<sub>3</sub>Al in the trimerization process did not influence the productivity. With the use of the supported catalyst, products could be isolated via simple filtration. The extended longevity and ease of operation are important advantages of the supported catalyst.

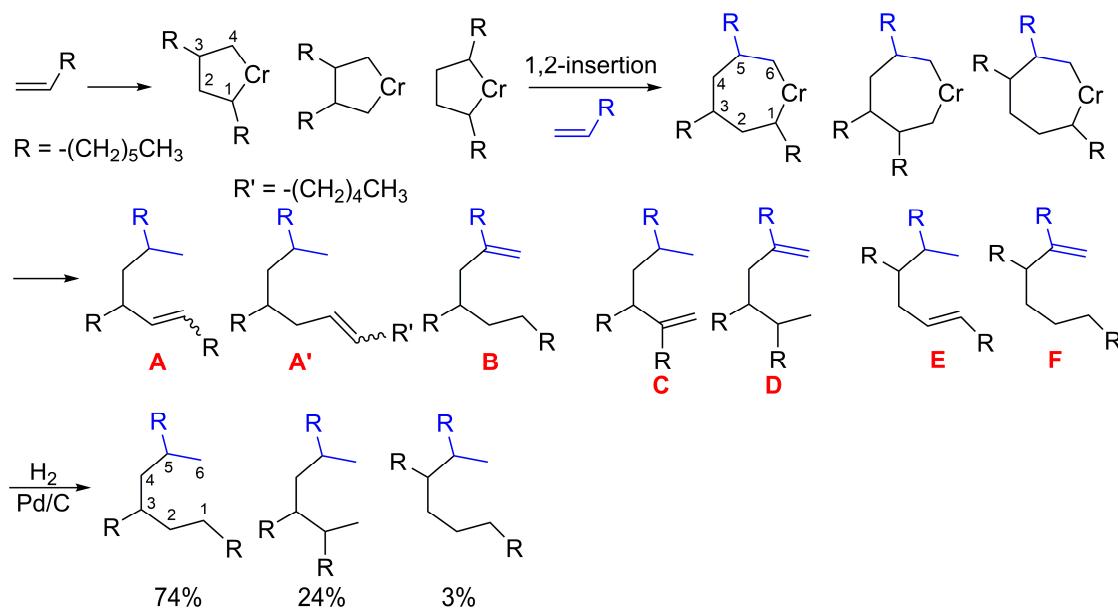


**Figure 2.** Conversion vs. time at various temperatures.

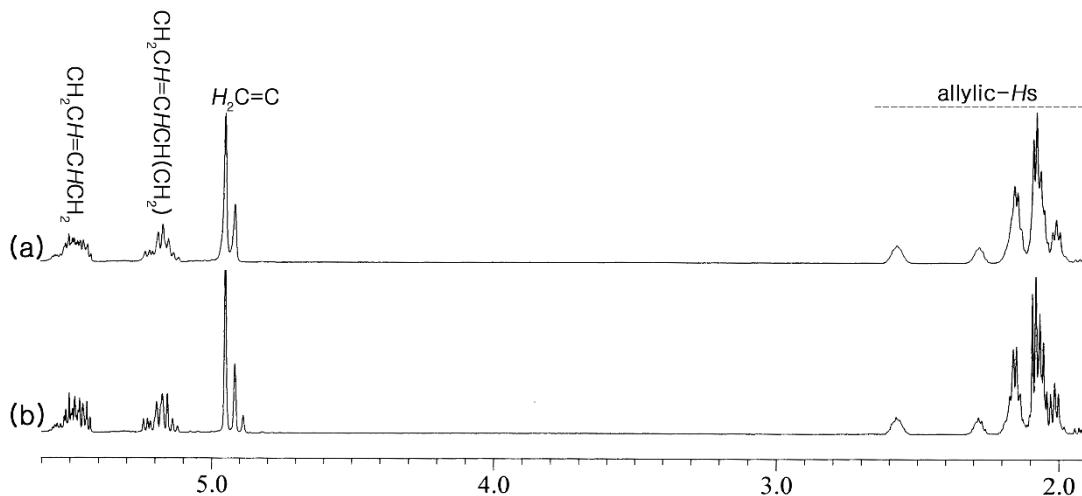
A small amount of dimer was formed along with the major trimer, while other oligomers higher than the trimer were not observed in simulated distillation gas chromatography (SimDis GC) analysis; that is, 0.02, 0.07, and 0.87 wt.% dimers were observed with 44, 59, and 64 wt.% main product trimer when oligomerization was performed for 72 h at ~25, 40, and 60 °C, respectively (Table S2). However, the amount of dimer generated was significant at 80 °C (5.0 wt.% at an equivalent reaction time of 72 h). The isomerization of 1-octene to 2-octene was also significant at 80 °C, wherein 20 wt.% of 1-octene was converted to 2-octene within 72 h (Figure S1). The isomerization side reaction was not severe at ~25, 40, and 60 °C, with only 0.8, 1.3 and 3.1 wt.% of 1-octene being converted to 2-octene, respectively, at a reaction time of 72 h.

The microstructure of the trimer generated with the homogenous Cr catalyst was thoroughly investigated by quantitative <sup>13</sup>C NMR spectroscopy using <sup>13</sup>C labeled samples by Köhn, and the results are shown in Scheme 1 [23,27]. The isomer distribution of trimers prepared with homogeneous [(pentyl)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>TAC]CrCl<sub>3</sub> catalyst was reported to be: ~60% of A (possibly including A'),

~12% of **B**, ~17% of **C**, ~4% of **D**, ~3% of **E**, and ~1% of **F**. In the  $^1\text{H}$  NMR spectrum of trimer generated at  $\sim 25^\circ\text{C}$ , three vinylic signals were observed at 5.58–5.42, 5.26–5.11, and 4.97–4.90 ppm with integration ratios of 1.0:0.86:1.43 (Figure 3) [27]. The first two signals were assigned to  $-\text{CH}_2\text{CH}=\text{CHCH}_2-$  (**A'** in Scheme 1) and  $-\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_2)-$  (**A**), respectively, and the third was assigned to  $\text{H}_2\text{C}=\text{C}(\text{CH}_2)\text{CH}_2-$  (**B** and **D**) and  $\text{H}_2\text{C}=\text{C}(\text{CH}_2)\text{CH}(\text{CH}_2)-$  (**C**) [23]. The allylic proton signals  $-\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_2)-$  in **A**,  $-\text{CH}_2\text{CH}=\text{CHCH}_2-$  in **A'**,  $\text{H}_2\text{C}=\text{C}(\text{CH}_2)\text{CH}_2-$  in **B** and **D**, and  $\text{H}_2\text{C}=\text{C}(\text{CH}_2)\text{CH}(\text{CH}_2)-$  in **C** were observed in the region of 2.7–2.0 ppm. The sum of the integration values of the allylic proton signals agreed well with the integration values of the vinylic proton signals based on the reported product distribution and aforementioned assignment (i.e.,  $I_{2.7-2.0} = 2.0 \times I_{5.58-5.42} + 1.5 \times I_{5.26-5.11} + 1.5 \times I_{4.97-4.90}$ , where  $I$  is the integration value in the region of the subscript numbers). The  $^1\text{H}$  NMR spectrum of trimer generated at  $40^\circ\text{C}$  was almost identical to that of the trimer generated at  $\sim 25^\circ\text{C}$ . In the  $^1\text{H}$  NMR spectra of trimer generated at  $60^\circ\text{C}$ , a new singlet signal was additionally observed in the vinylidene ( $\text{H}_2\text{C}=\text{C}$ ) region at 4.89 ppm (Figure 3). However, the integration ratio of the three vinyl signals remained unaltered at the three temperatures (i.e.,  $I_{5.58-5.42}:I_{5.26-5.11}:I_{4.97-4.87} = 1.0:0.83:1.42$ ).

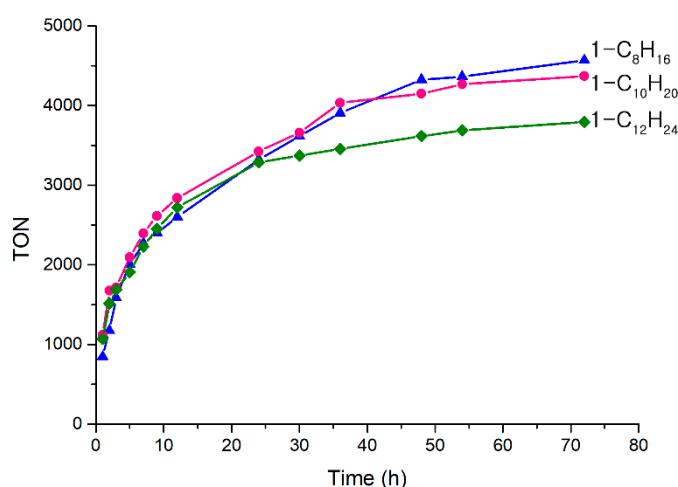


**Scheme 1.** Rationale for the observed trimer isomer distribution.



**Figure 3.**  $^1\text{H}$  NMR spectra of 1-octene trimer generated at (a)  $25^\circ\text{C}$  and (b)  $60^\circ\text{C}$ .

The reactivity of 1-decene and 1-dodecene was investigated and compared with that of 1-octene by performing the oligomerization at 60 °C under an identical catalyst feed (400-mg supported catalyst/20-g neat monomer) and monitoring the conversion over time (Figure S2 and Table S3). The use of 1-decene provided 77% conversion (TON, 4400) within a reaction time of 72 h, which is significantly higher than that observed with 1-octene (64% within 72 h; TON, 4600). The conversion was further improved with the employment of 1-dodecene (80% within 72 h; TON, 3800). After reaching 70% conversion in 24 h, the reaction rate slowed down severely, requiring another 48 h to reach 80% conversion. This is in accordance with lowering monomer concentration at the stage of high conversion. However, in the plot of TON vs. time (Figure 4), the three lines representing 1-octene, 1-decene, and 1-dodecene overlap each other up to a reaction time of 24 h, which indicates that monomer reactivity is comparable for all three  $\alpha$ -olefins. The  $^1\text{H}$  NMR signal patterns of vinylic and allylic protons and the integration value ratios of the three vinylic signals (i.e.,  $I_{5.58–5.42}$ :  $I_{5.26–5.11}$ :  $I_{4.97–4.87}$ ) were identical for all the three samples of 1-octene-, 1-decene-, and 1-dodecene-generated trimers (Figure S3).



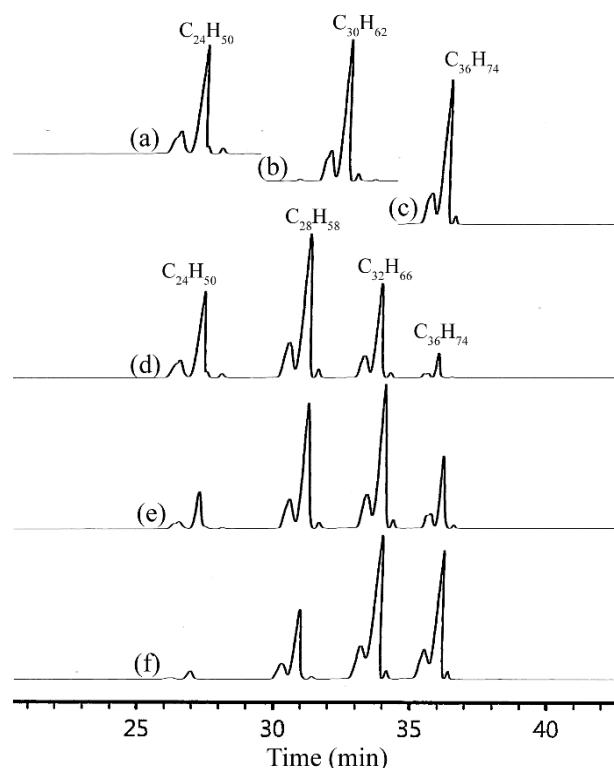
**Figure 4.** Turnover number (TON) vs. time for various monomers.

### 2.3. Preparation of $\alpha$ -olefin Trimers and Lubricant Properties

To evaluate lubricant properties of trimers, ~200 g of  $\alpha$ -olefin trimers was prepared using the supported catalyst. Thus, 1-octene, 1-decene, and 1-dodecene monomers (300 g), as well as 1-octene/1-dodecene mixed monomers (300 g) in 2/1, 1/1, and 1/2 mole ratios were stirred for 72 h at 60 °C under neat conditions in the presence of the optimized supported catalyst (6.0 g, MAO-g/silica-g = 0.45, Al/Cr = 84). Conversions exceeding 60% were attained in all cases. After oligomerization, the catalyst could be completely removed by filtration. After removing the unreacted monomer by vacuum distillation, the hydrogenation reaction was performed under neat conditions without feeding an additional solvent, using a Pd/C catalyst (0.5 wt.% per trimer) under 25 bar H<sub>2</sub> gas at rt for 12 h. Complete hydrogenation was confirmed by  $^1\text{H}$  NMR spectral analysis, wherein a complete disappearance of vinylic and allylic signals was observed after hydrogenation (Figure S4).

The prepared  $\alpha$ -olefin oligomers were analyzed by a SimDis GC (Figure 5). Selective generation of trimer was evident; a set of signals assignable to the trimers (i.e., C<sub>24</sub>H<sub>50</sub>, C<sub>30</sub>H<sub>62</sub>, and C<sub>36</sub>H<sub>74</sub>) was observed predominantly in the cases of 1-octene, 1-decene, and 1-dodecene trimerization (Figure 5a–c). Each set of signals was composed of three signals in a ratio of 74 : 24 : 3, which is in good agreement with the trimer isomer distribution results revealed by quantitative  $^{13}\text{C}$  NMR spectroscopy using  $^{13}\text{C}$  labeled samples [27]. Hydrogenation of the isomers of A (possibly including A', ~60%) and B (~12%), derived from 1,3,5-alkyl-substituted chromacycloheptane, which is, in turn, derived from 1,3-alkyl-substituted chromacyclopentane, resulted in the generation of 1,3,5-alkyl-substituted hexane as the major product (~72%) (Scheme 1). Hydrogenation of the isomers of C (~17%) and D (~4%), derived from 2,3,5-alkyl-substituted chromacycloheptane via

1,2-insertion, which is, in turn, derived from 2,3-alkyl-substituted chromacyclopentane, results in the generation of the second major isomer, 2,3,5-alkyl-substituted hexane (~21%). Hydrogenation of the isomers of E (~3%) and F (~1%), derived from 1,4,5-alkyl-substituted chromacycloheptane, which is, in turn, derived from 1,4-alkyl-substituted chromacyclopentane, results in the generation of a minor product, 1,4,5-alkyl-substituted hexane (~4%). The ratios of the three signals (i.e., signals for 1,3,5-alkyl-, 2,3,5-alkyl-, and 1,4,5-alkyl-substituted hexane) were the same for 1-octene, 1-decene, and 1-dodecene trimers (74:24:3).



**Figure 5.** Simulated distillation Gas Chromatography (SimDis GC) charts for  $\alpha$ -olefin trimers prepared with (a) 1-octene, (b) 1-decene, and (c) 1-dodecene monomers, as well as 1-octene/1-dodecene mixed monomers in (d) 2:1, (e) 1:1 and (f) 1:2 mole ratios.

Four fractions were observed for the samples prepared with 1-octene/1-dodecene mixed monomers. The four fractions corresponded to  $C_{24}H_{50}$  (trimer of three 1-octene units),  $C_{28}H_{58}$  (trimer of two 1-octene and one 1-dodecene),  $C_{32}H_{66}$  (trimer of one 1-octene and two 1-dodecene), and  $C_{36}H_{74}$  (trimer of three 1-dodecene). As previously mentioned, monomer reactivity did not differ between 1-octene and 1-dodecene, and the molar ratio of the four fractions (i.e.,  $C_{24}H_{50} : C_{28}H_{58} : C_{32}H_{66} : C_{36}H_{74}$ ) can be estimated by statistics. The estimated ratios were in good agreement with the ratios measured on SimDis GC; for example, for the sample prepared in a 2:1 molar ratio of 1-octene/1-dodecene (Figure 5d), the estimated  $C_{24}H_{50} : C_{28}H_{58} : C_{32}H_{66} : C_{36}H_{74}$  molar ratios are 0.296:0.444:0.222:0.037 (i.e.,  $0.67 \times 0.67 \times 0.67 : 3 \times 0.67 \times 0.67 \times 0.33 : 3 \times 0.67 \times 0.33 : 0.33 \times 0.33 \times 0.33$ ), while the ratios measured by SimDis GC were 0.26:0.45:0.21:0.04 (Table S4). In each fraction, three isomer signals were observed with ratios similar to those of 1-octene, 1-decene, and 1-dodecene trimer signals (74:24:3; Table S4).

Lubricant properties (kinematic viscosity at 40 and 100 °C, viscosity index, and pour point) were measured for samples prepared on a ~200 g scale at a certified institute (entries 1–6 in Table 1). The properties of commercial-grade PAOs (PAO-2.0, PAO-2.5, and PAO-4.0), fractionated in the cationic oligomerization process of 1-decene, were also measured for comparison (entries 7–9). The measured values of kinematic viscosity at 40 and 100 °C, viscosity index, and pour point for commercial-grade PAOs were in agreement with the literature values. However, the measured values for 1-decene trimers

(kinematic viscosity at 40 °C, 15.1 cSt; kinematic viscosity at 100 °C, 3.9 cSt; viscosity index, 161) differed appreciably from reported data (kinematic viscosity at 40 °C, 12.1–13.8 cSt; kinematic viscosity at 100 °C, 3.1–3.4 cSt; viscosity index 125–137), which had been measured for samples prepared on a small scale (<10 g), at a low temperature (0 °C), using various homogeneous [R<sub>3</sub>TAC]CrCl<sub>3</sub> catalysts [24]. The higher the viscosity index, the less the viscosity is affected by changes in temperature, and the better a lubricant base oil will be. With a marginal increase in the viscosity index relative to that of PAO-4.0, which is fractionated in the cationic oligomerization process of 1-decene (125–137 vs. 124), 1-decene trimers, selectively generated via a metallacyclic intermediate, have been regarded negatively as a lubricant base oil [1]. However, the viscosity index measured herein for 1-decene trimers, prepared on a relatively large scale with the supported chromium catalyst, was significantly higher than that of the commercial-grade PAO-4.0 (161 vs. 123). The kinematic viscosity and viscosity index gradually increased with the switch from the 1-octene trimer to the 1-decene trimer and further to the 1-dodecene trimer (entries 1–3). The pour point of 1-octene and 1-decene trimers was sufficiently below the instrument limiting value (<−57 °C), while that of 1-dodecene trimer was disadvantageously high at −39 °C.

**Table 1.** Lubricant properties of prepared  $\alpha$ -olefin trimers and commercial-grade poly( $\alpha$ -olefin)s (PAOs).

Entry	Monomer	Kinematic Viscosity at 40 °C (cSt)	Kinematic Viscosity at 100 °C (cSt)	Viscosity Index	Pour Point (°C)
1	1-C <sub>8</sub> H <sub>16</sub>	8.13	2.4	110	<−57
2	1-C <sub>10</sub> H <sub>20</sub>	15.1	3.9	161	<−57
3	1-C <sub>12</sub> H <sub>24</sub>	21.6	5.0	171	−39
4	1-C <sub>8</sub> /1-C <sub>12</sub> (2 : 1)	11.5	3.0	122	<−57
5	1-C <sub>8</sub> /1-C <sub>12</sub> (1 : 1)	14.7	3.6	137	<−57
6	1-C <sub>8</sub> /1-C <sub>12</sub> (1 : 2)	16.5	4.1	160	−51
7	PAO-2.0 (1-C <sub>10</sub> )	4.98	1.7	93	<−57
8	PAO-2.5 (1-C <sub>10</sub> )	7.71	2.3	109	−51
9	PAO-4.0 (1-C <sub>10</sub> )	17.4	3.9	123	<−57

It has also been demonstrated that a courier prepared with a 1-octene/1-dodecene mixed monomer exhibited lubricant properties similar to those prepared with 1-decene; for example, the trimer prepared with a 1:2 1-octene/1-dodecene monomer mix exhibited lubricant properties comparable to those of 1-decene trimer (kinematic viscosity at 40 °C, 16.5 vs. 15.1 cSt; kinematic viscosity at 100 °C, 4.1 vs. 3.9 cSt; viscosity index, 160 vs. 161), although the pour point was inferior (−51 °C vs. <−57 °C ; entry 6 vs. entry 2). Lubricant properties could also be tuned by varying the 1-octene/1-dodecene molar ratio, wherein viscosity as well as viscosity index increased with a decrease in the 1-octene/1-dodecene ratio (entries 4 and 5). Superior lubricant base oils may be obtained by fractionation of the four fractions generated in the selective trimerization of 1-octene/1-dodecene mixed monomers.

### 3. Material and Methods

#### 3.1. Materials

All manipulations were performed in an inert atmosphere using standard glove box and Schlenk techniques. Toluene and hexane were purchased from ThermoFischer Scientific (Seoul, Korea), purified over Na/ketyl, distilled, and stored under N<sub>2</sub> gas. 1-Octene, 1-decene, and 1-dodecene were purchased from SigmaAldrich (Seoul, Korea) and purified by passing through an activated alumina column, dried over Na/K alloy, distilled, and stored under N<sub>2</sub> gas prior to use. MAO (10 wt.% in toluene; 4.6 wt.-%-Al) and silica (SYLOPOL-2410) were purchased from Grace (Yeosu, Korea). <sup>1</sup>H NMR (600 MHz) spectra were recorded using a JEOL ECZ 600 spectrometer. SimDis GC analysis was performed using a YL instrument 6500 GC (Seoul, Korea) system equipped with a DB-2887 column (10 m × 0.53 mm × 3  $\mu$ m; purchased from Agilent) and a flame ionization detector (FID). Lubricant properties of  $\alpha$ -olefin trimers and PAO were measured at K-petro Korea (Cheongju, Korea) according to ASTM D445-18, ASTM D2270-10 (2016), and ASTM D6749-02 (2012).

### 3.2. Preparation of Supported Catalyst

MAO (10 wt.% in toluene, 25 g, 43 mmol Al) was added to a flask containing silica (SYLOPOL-2410, 5.0 g) suspended in toluene (10 mL). The mixture was heated to 70 °C and stirred for 3 h. The solid was collected by filtration and washed with toluene (10 mL × 3) and hexane (20 mL × 2). The residual solvents were completely removed using a vacuum line to obtain a white powder (MAO-silica, 7.4 g). The prepared MAO-silica (16.0 g),  $(C_{12}H_{25})_3TAC$ CrCl<sub>3</sub> (0.800 g, 1.07 mmol), and toluene (80 mL) were added to a flask, and the resulting suspension was stirred for 2 h at rt. The solid was collected by filtration and washed with toluene (50 mL) and hexane (30 mL). The filtrate was colorless, indicating that the chromium complex was completely anchored. Residual solvents were removed using a vacuum line to obtain a green powder (16.6 g, 64 µmol Cr/g-cat, Al/Cr = 84). The prepared supported catalyst was dispersed in toluene (3.5 g) and aqueous nitric acid (7.0 g, 10 wt.%) was added. After stirring overnight, aqueous phase was taken for inductively coupled plasma (ICP) analyses, through which the Al and Cr contents were determined.

### 3.3. 1-Octene Trimerization on A Small Scale for the Data in Figures 2 and 3

A Schlenk flask (50 mL size) was charged with the prepared supported catalyst (400 mg) and 1-octene (20 g). The flask was sealed with a Teflon valve and immersed in an oil bath with a temperature set to r.t (~25 °C), 40 °C, 60 °C, and 80 °C. During the reaction, a small amount of solution (200 mg) was sampled for SimDis GC analysis.

### 3.4. Preparation of $\alpha$ -Olefin Trimer on a Large Scale for the Samples in Table 1

A Schlenk flask (1 L size) was charged with the supported catalyst (6.0 g), 1-octene (120 g), and 1-dodecene (180 g). After the flask was sealed with a Teflon valve, it was immersed in an oil bath with a temperature of 60 °C. After 72 h had elapsed, the resulting mixture was filtered. The filtrate was distilled at 80 °C under vacuum to remove unreacted monomers. A colorless residue was obtained (207 g, 69% conversion), which was transferred to a bomb reactor (2 L size) containing a Pd/C catalyst (1.0 g, 10 wt.-%Pd). The reactor was pressurized with 25 bar H<sub>2</sub> gas and stirred for 12 h at room temperature. After venting off H<sub>2</sub> gas, the Pd/C catalyst was removed by filtration over Celite to obtain a colorless oil, which was used without further treatment for the measurement of lubricant properties.

### 3.5. SimDis GC Analysis

A sample (200 mg) drawn from the reaction was diluted with nonane (300 mg) and syringe-filtered (pore size, 0.2 µm). The filtrate (2 µL) was injected into a GC equipped with a DB-2887 column. N<sub>2</sub> gas flowed at a constant rate (10 mL/min). The inlet and FID temperatures were set to 320 °C. The oven temperature was controlled by holding at 40 °C for 4 min, increasing to 200 °C at a rate of 10 °C/min, holding at 200 °C for 4 min, increasing to 320 °C at a rate of 10 °C/min, and finally holding at 320 °C for 6 min.

## 4. Conclusions

$(N,N',N''\text{-tridodecyltriazacyclohexane})\text{CrCl}_3$  complex was reacted with MAO-silica for the preparation of a supported catalyst. By the immobilization of the chromium catalyst on the silica surface, the deactivation process was diminished and the activity was sustained, although it decreased gradually with time. After 72 h, even at an elevated temperature of 60 °C, the supported catalyst provided 60–80% conversion (TON, 3800–4600), enabling the preparation of  $\alpha$ -olefin trimers on ~200 g scale, while the corresponding homogeneous catalyst was completely deactivated within 3 h at 60 °C. SimDis GC analysis performed after hydrogenation confirmed the selective generation of trimers. Each trimer signal was split into three signals, in all cases, in a ratio of ~74:~24:~3, which were assigned to 1,3,5-, 2,3,5-, and 1,4,5-alkyl-substituted hexanes. Because of the simplified skeleton, the prepared 1-decene trimer displayed superior lubricant properties compared to those of commercial-grade PAO-4,

produced via the cationic oligomerization of 1-decene. 1-Octene/1-dodecene mixed couriers were also prepared, and SimDis GC analysis indicated that the ratio of C<sub>24</sub>H<sub>50</sub>, C<sub>28</sub>H<sub>58</sub>, C<sub>32</sub>H<sub>66</sub>, and C<sub>36</sub>H<sub>74</sub> fractions was statistically controlled according to the variation in 1-octene/1-dodecene feed ratios. A mixed courier prepared with the 1-octene/1-dodecene mixed monomer exhibited lubricant properties comparable to those of the 1-decene trimer, although the pour point was inferior. The activity of the reported catalyst (TON, ~4000) is unfortunately inadequate for application in a commercial process. However, this study offers valuable insights for the future development of catalysts with higher activity for selective  $\alpha$ -olefin trimerization, which could have a substantial impact on the commercial production of lubricant base oils.

## 5. Patents

A patent was filed (KR. Patent 10-1449474, 13 Oct 2014, assigned to Ajou University) and a patent was applied (Kr 10-2020-0061874, 22 May 2020, assigned to Ajou University).

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/10/9/990/s1>, Table S1. 1-Octene trimerization at various temperatures (data for Figure 2), Table S2. Trimer/dimer selectivity in 1-octene trimerization performed at various temperature (Figure 2), Table S3. Trimerization of 1-octene, 1-decene, and 1-dodecene performed at 60 °C (Figure 4), Table S4. SimDis GC data for 1-octene/1-dodecene mixed trimerization reactions, Figure S1: SimDis GC chart for 1-octene trimerization performed at 80 °C for 72 h, Figure S2: Conversion vs. time for 1-octene, 1-decene, and 1-dodecene trimerization performed at 60 °C, Figure S3. <sup>1</sup>H NMR spectra of 1-octene, 1-decene, and 1-dodecene trimmers, Figure S4. <sup>1</sup>H NMR spectra before and after hydrogenation of 1-octene trimer.

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