

Synthesis of Synthetic Lubricants by Trimerization of 1-Decene and 1-Dodecene with Homogeneous Chromium Catalysts

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Abstract: The Cr-catalyzed trimerization of 1-decene and 1-dodecene is a highly selective method to synthesize C₅₀ and C₅₆ olefins. After hydrogenation, these products display very attractive viscosity indices (VI's). Due to the high trimer selectivity of the reaction no additional work-up is needed to separate

C₂₀, C₂₄ or C₄₀₊ oligomers from the product prior to a potential use of these products in synthetic lubricants for automotive applications.

Keywords: alkene; chromium; lubricants; trimerization; viscosity

Introduction

Modern synthetic lubricants for high purpose uses have to fulfill many requirements. Among others, industry asks for low pour points, low vapor pressure and good lubricating properties at reasonable prices. Of particular interest are low viscosities to lower friction and a high viscosity index (VI). The VI, calculated by an empirical formula, reflects the dependence of the viscosity on the temperature: the less significant this dependency the higher is the VI.^[1]

These requirements are fulfilled by C₅₀–C₄₀ alkanes with a certain degree of branching.^[1] The synthesis of these compounds is carried out industrially by cationic oligomerization (e.g., with BF₃/methanol as catalyst^[2]) using 1-decene as feedstock followed by hydrogenation of the obtained oligomers. However, the products obtained in this process contain besides C₅₀ and C₄₀ oligomers significant amounts of dimers and pentamers. Both side products decrease the lubricant's quality. Dimer products add significant vapor pressure and the presence of pentamers increases the pour point of the material. Another decrease of the VI arises from skeleton isomerization that is observed as a side reaction of the cationic oligomerization.

It is well known that homogeneous Cr catalysts formed by *in situ* reaction of a Cr(III) salt, pyrrole and alkylaluminum species are able to trimerize ethylene to 1-hexene with high selectivity.^[3,4] These

catalytic systems also convert mixtures of ethylene and 1-olefins into mixtures of cotrimerization products but show no activity for the trimerization of higher 1-olefins alone (> C₅).^[5]

Results and Discussion

In contrast, we report here that Cr complexes with N,N',N''-trialkyltriaza-cyclohexane ligands of the general formula (R₃TAC)CrCl₃ (as shown in Figure 1) are highly selective catalysts for the trimerization of 1-decene and 1-dodecene after activation with MAO. These Cr complexes can be synthesized, for example, by reaction of CrCl₃ with R₃TAC in presence of catalytic amounts of Zn and have been characterized by UV-Vis spectroscopy, ²H NMR spectroscopy and X-ray analysis.^[6,7]

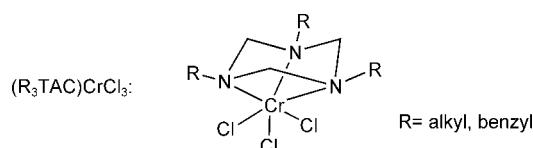


Figure 1. Cr complexes of general formula (R₃TAC)CrCl₃ as used for the trimerization of 1-decene and 1-dodecene

Ligand Influence

Exemplified for the trimerization of 1-dodecene, the influence of the applied R_5TAC ligand on the reactivity of the catalytic system is presented in Table 1. The experiments reveal a significant dependence of catalytic activity and trimerization/isomerization ratio on the nature of the alkyl substituent R.

After reaction, some unconverted 1-dodecene, linear C_{12} olefins with an internal double bond (products of olefin isomerization) and C_{56} olefins were detected by GC in the reaction mixture. In all cases, the amount of C_{24} dimers and higher oligomers (C_{48+}) was found to be very low (<0.5 mass % of the overall reaction mixture for all catalytic runs at 0 °C) indicating a very high trimer selectivity of the oligomerization reaction. Schematically, the reactivity of the catalytic 1-dodecene transformation with $[(R_5TAC)CrCl_5]/MAO$ can be described as shown in Figure 2.

With regard to the trimerization/isomerization ratio, it is noteworthy that a higher degree of branching of the alkyl group R in the α -position enhances the undesired isomerization reaction (entry 4 in Table 1). Moreover, it is important to mention that the catalyst

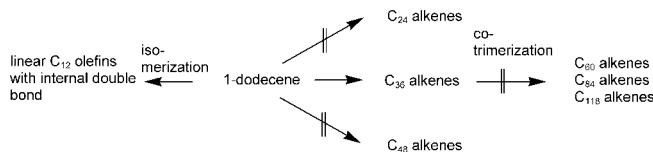


Figure 2. Reactivity of 1-dodecene using $[(R_5TAC)CrCl_5]/MAO$ as catalytic system.

Table 1. Trimerization of 1-dodecene – influence of the alkyl group R of the R_5TAC -ligands on catalytic reactivity and selectivity.

Entry	Ligand	Conversion [%]	$S(C_{56})$ [%] ^[a]	$S(iso-C_{12})$ [%] ^[b]	TON ^[c]
1	$(Do)_5TAC$ ^[d]	97.7	81.0	19.0	724
2	$(1,5-Me_2Hex)_5TAC$ ^[d]	76.5	85.7	14.5	677
3	$(2-Et-Hex)_5TAC$ ^[d]	80.5	93.0	7.0	1026
4	$(1,1-Me_2Un)_5TAC$ ^[d]	85.8	6.5	93.5	50
5	$(MeBz)_5TAC$ ^[d]	45.9	69.0	31.0	285

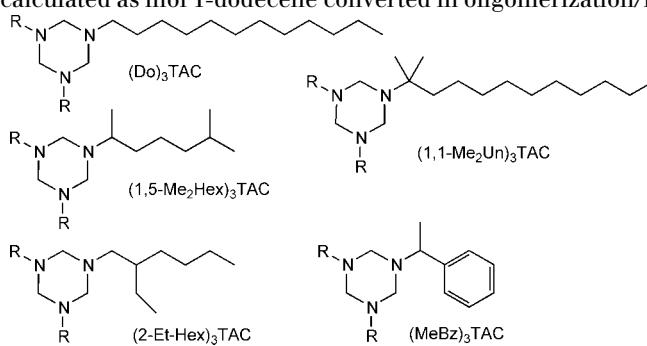
General conditions: about 10 mL 1-dodecene, 10 mL toluene, 0.05 mmol $[(R_5TAC)CrCl_5]$, 5 mmol MAO, 20 h, 0 °C.

^[a] Selectivity to C_{56} products calculated as amount of C_{56} in all products;

^[b] Selectivity of linear, internal C_{12} olefins calculated as amount of linear, internal C_{12} olefins in all products;

^[c] Turnover number calculated as mol 1-dodecene converted in oligomerization/mol Cr catalyst.

^[d] Ligand structures:



is sensitive towards elevated temperatures. Typically, the oligomerization reactions are carried out at 0 °C in aromatic or aliphatic hydrocarbon solvents (e.g., toluene or heptane). Another option is to use the feedstock as solvent. However, in this case the limited solubility of the catalyst in the feedstock causes certain restrictions.

Figure 3 shows kinetic investigations of the 1-dodecene trimerization with different R_5TAC ligands. In all cases an induction period is observed at the beginning of the reaction. Nevertheless, the main reactivity occurs within the first five hours of the reaction. Later the oligomerization activity slows very much down even if in some cases the level of conversion is still far from completion. Obviously, the Cr catalyst deactivates after a certain reaction time. However, ligand

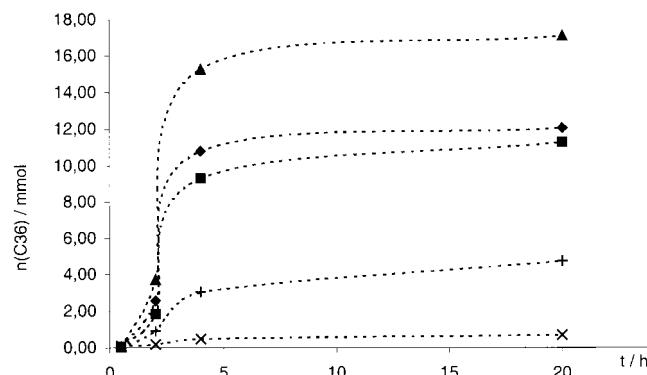


Figure 3. Trimerization of 1-dodecene – kinetic investigations using different R_5TAC ligands. $[(Do)_5TAC]$: –◆–; $(1,5-Me_2Hex)_5TAC$: –■–; $(2-Et-Hex)_5TAC$: –▲–; $(1,1-Me_2Un)_5TAC$: –+–; $(MeBz)_5TAC$: –×–.

decomposition can be excluded since no degradation products could be observed by GC analysis. A possible deactivation mechanism by product inhibition has been investigated as well. However, experiments with added trimer product from other catalytic runs at the start of the reaction could not confirm this hypothesis.

Mechanistic Aspects

The high selectivity of the trimerization reaction is based on the special mechanism of the reaction (as shown in Figure 4, here with 1-decene as feedstock).^[7] The catalytic reaction proceeds following a metallacycle mechanism with five- and seven-membered Cr metallacycles being the key-intermediates. From the latter the trimer product olefin is eliminated. In contrast, the five-membered metallacycle does not allow olefin elimination. Therefore no formation of dimer products is observed. Since elimination from the seven-membered metallacycle is significantly faster than additional 1-decene insertion, the amount of tetramers and higher oligomers is very low as well.

The olefins formed are either internal (RHC=CHR) or vinylidenes (H₂C=CR₂). No 1-olefins are observed in the trimer fraction. Since comparative experiments reveal that the Cr catalyst only converts 1-olefins it becomes understandable that no consecutive cotrimmerization is found.

No skeleton isomerization of feedstock or product could be observed. Consequently, only four different

trimer products should be obtained after hydrogenation according to the mechanism displayed in Figure 4. In fact, four main products are found in the trimer fraction after hydrogenation which account for more than 95% of all trimers (the side products may be explained by incomplete hydrogenation). Depending on the Cr complex under investigation the distribution of the four regioisomers can vary significantly. However, to date no clear assignment of the different GC peaks to individual regioisomers has been possible.

Viscosity of the Products

The viscosity and – even more important – the temperature dependence of the viscosity (VI) is critical for a potential use of the trimerization products in synthetic lubricants (after hydrogenation with Pd on carbon as catalyst). All trimerization samples showed Newtonian behavior in the viscosity determination. Selected results for the kinetic viscosities and the VI's (determined after ISO 2909) are presented in Table 2.

From the viscosity and VI determination the following statements can be derived: a) As expected, C₁₂ trimers (C₅₆ products) show higher absolute viscosity at 40 °C and 100 °C and higher VI's than C₁₀ trimers (C₅₀ products). b) All samples generated by Cr-catalyzed trimerization display equal or better VI's than commercial PAO 4 and PAO 6 samples (produced via the BF₃/co-catalyst system) even if absolute viscosities at 40 °C are lower in most cases (entries 4–8). c) Different alkyl groups R at the R₃TAC ligand seem to have only little effect on the VI of the product. However, aromatic substituents seem to have an enhancing effect on the VI of hydrogenated trimerization products (comparison of entries 6, 7 with entry 8). d) The use of Co-MAO activation instead of MAO activation seem to enhance the VI of the hydrogenated trimerization products. e) Pour points of all hydrogenated C₅₀ products are between –42 °C and –45 °C, pour point of the hydrogenated C₅₆ product (entry 3) is –30 °C.

Besides the attractive viscosity indices, it is expected that a significant technical advantage of the Cr-catalyzed trimerization of 1-decene and 1-dodecene vs. the well-known BF₃-catalyzed oligomerization^[2] arises from the high trimer selectivity of the reaction. Both dimers and pentamers decrease the quality of the product for a potential use in synthetic lubricants due to high volatility (C₂₀, C₂₄) and/or high pour point (C₅₀₊), respectively. Therefore, these components have to be either removed (dimers by distillation) or restricted in the conventional BF₃ process.

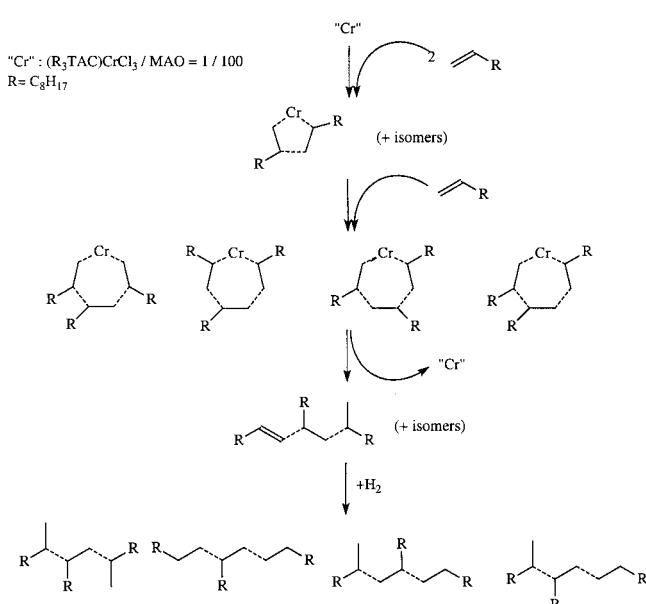


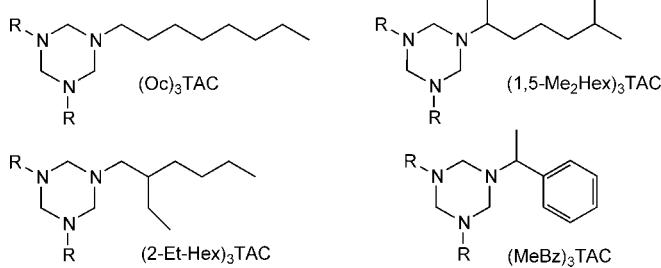
Figure 4. Mechanism of the Cr-catalyzed trimerization of 1-decene.

Table 2. Kinetic viscosities and VIs (after ISO 2909) of C₅₀ and C₅₆ alkanes obtained by C₁₀ and C₁₂ trimerization with [(R₅TAC)CrCl₅]/MAO followed by hydrogenation in comparison to commercial PAO 4 and PAO 6.^[a]

Entry	Ligand ^[b]	Co-catalyst	Product	Kinetic viscosity 40 °C/cSt	Kinetic viscosity 100 °C/cSt	VI
1			PAO 4	17.5	4.0	124
2			PAO 6	51.1	5.9	157
3	(1,5-Me ₂ Hex) ₅ TAC	MAO	C ₅₆	18.5	4.5	150
4	(1,5-Me ₂ Hex) ₅ TAC	MAO	C ₅₀	12.2	3.2	126
5	(Oc) ₅ TAC	MAO	C ₅₀	15.8	5.4	125
6	(1,5-Me ₂ Hex) ₅ TAC	Co-MAO	C ₅₀	11.8	3.1	150
7	(2-Et-Hex) ₅ TAC	Co-MAO	C ₅₀	15.0	5.3	151
8	(Bz) ₅ TAC	Co-MAO	C ₅₀	12.1	5.2	157

[a] Trimerization conditions for entries 3–8: 10 mL 1-alkene feedstock, 10 mL toluene, 0.05 mmol [(R₅TAC)CrCl₅], 5 mmol MAO or Co-MAO, 20 h, 0 °C; activity (turnover number) 1-decene trimerization/activity 1-dodecene trimerization (under identical conditions) = 1.5–1.7 (depending on the Cr complex used); activity (turnover number) MAO activation/Co-MAO activation (under identical conditions) = 1.7–1.9 (depending on the Cr complex used).

[b] Ligand structures:



Conclusions

In summary, we have shown that a highly selective trimerization of 1-decene and 1-dodecene can be carried out with catalytic systems of the general type [(R₅TAC)CrCl₅]/MAO (R = alkyl, aryl). The reaction conditions are important in order to avoid thermal decomposition of the catalyst and to ensure complete solubility of the active catalyst. After hydrogenation, the products may be interesting components of synthetic lubricants since they display appropriate viscosity and attractive VI's.

Experimental Section

General Remarks

All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated by conventional methods prior to use. 1-Olefins were purchased from Fluka, distilled and stored under argon. MAO and Co-MAO (10% *iso*-butylmethylalumoxane in heptane) solutions were used as purchased from WITCO. *N,N',N''*-Tribenzyltriazacyclohexane was purchased from Aldrich. *N,N',N''*-Tris(octyl)triazacyclohexane and *N,N',N''*-tris(dodecyl)triazacyclohexane and their chromium complexes were prepared as described earlier.^[7a]

General Procedure for the Synthesis of R₅TAC Ligands

Paraformaldehyde was added to a solution of freshly distilled amine in toluene at room temperature and the reaction mixture was heated to reflux for 30 min. The formed water was removed in an azeotropic distillation with the toluene solvent. The crude product was dried under vacuum and used without further purification in the complexation step.

N,N',N''-Tris(1,5-dimethylhexyl)triazacyclohexane: 2-Amino-5-methylheptane (3.911 g, 30.26 mmol) was reacted with paraformaldehyde (0.956 g, 30.26 mmol) in 15 mL toluene. *N,N',N''-Tris(1,5-dimethylhexyl)triazacyclohexane* was isolated; yield: 3.85 g (91%). ¹H NMR (200 MHz, CDCl₃): δ = 3.47 (br. s, 6 H, N-CH₂-N), 2.65 (br. s, 3 H, N-CH-), 1.0–1.6 (21 H), 0.96 (d, 6.2 Hz, 9 H), 0.81 (d, 6.4 Hz, 18 H); ¹³C NMR (CDCl₃): δ = 15.9, 22.4, 22.5, 24.1, 27.8, 34.2, 39.1, 54.4, 67.7.

N,N',N''-Tris(2-ethylhexyl)triazacyclohexane: 2-Ethylhexylamine (2.04 g, 15.78 mmol) was reacted with paraformaldehyde (0.499 g, 15.78 mmol) in 7.5 mL toluene. *N,N',N''-Tris(2-ethylhexyl)triazacyclohexane* was isolated as a clear and colorless oil; yield: 1.9 g (85%). ¹H NMR (300 MHz, CDCl₃): δ = 3.19 (br, 6 H, N-CH₂-N), 2.19 (d, 6 H, N-CH₂-), 1.2–1.27 (m, 24 H, -CH₂-), 0.76–0.82 (two t, 18 H, -CH₃); ¹³C NMR: (100 MHz, CDCl₃): δ = 11.0, 14.4, 23.4, 24.9, 29.2, 31.7, 37.6, 57.0, 75.5.

N,N',N''-Tris(S-methylbenzyl)triazacyclohexane: S-1-Phenylethylamine (21.88 g, 181 mmol) was reacted with paraformaldehyde (5.17 g, 172 mmol) in 30 mL of toluene. Recrystallization from hexane afforded *N,N',N''-tris(S-methylbenzyl)triazacyclohexane*; yield: 19.0 g (83%). ¹H NMR (200 MHz, CDCl₃): δ = 7.17–7.29 (m, 15 H, Ph), 3.72 (q, *J* = 6.7 Hz, 3 H, N-CH-), 3.59 (br, 6 H, N-CH₂-N), 1.29 (d, 6.7 Hz, 9 H, Me); ¹³C NMR (CDCl₃): δ = 20.1, 59.4, 70.0, 126.7, 127.5, 128.1, 144.3.

Synthesis of Cr Complexes $[(R_5TAC)CrCl_3]$ with R=benzyl, n-octyl, n-dodecyl, 1,5-dimethylhexyl, 2-ethylhexyl, S-methylbenzyl

Anhydrous $CrCl_3$ was suspended in toluene and 10 mg Zn was added. A solution of 1 equivalent of R_5TAC ligand in toluene was added and the reaction mixture was heated to reflux for 60 min. The product formation was observed by the deep violet color of the reaction mixture. The solvent was removed under vacuum and the crude product was dissolved in CH_2Cl_2 for further purification by column chromatography (column material: Silica 80 A; load 1 g crude product per 200 mL silica). After chromatography a deep violet solution was obtained. After removal of the CH_2Cl_2 under vacuum the residue was stirred in *n*-pentane to obtain the product as a crystalline powder.

[N,N',N''-Tris(1,1-dimethylundecyl)triazacyclohexane]CrCl₃: Paraformaldehyde (373 mg, 12.4 mmol) was added at 20 °C to 1,1-dimethylundecylamine (2.6 g, 12.4 mmol) dissolved in 15 mL toluene. To fully dissolve the aldehyde, the mixture was heated shortly to 50 °C. After cooling down to 20 °C the sample was stirred for 20 h. The solvent was removed and the *N*-methylidine-1,1-dimethylundecylamine was dried under vacuum; yield: 2.5 g (90%). ¹H NMR ($CDCl_3$): δ = 0.82 (tr, J = 6.7 Hz, 3 H), 1.07 (s, 6 H), 1.19 (br. s, 16 H), 1.43 (m, 2 H), 7.26 (d, J = 2.0 Hz, 2 H); ¹³C NMR ($CDCl_3$): δ = 147.7, 60.6, 42.85, 31.79, 30.08, 29.52, 29.23, 26.32, 23.93, 22.55, 13.95.

The imine (1.61 g, 7.16 mmol, 2.8 equivalents) was dissolved in 10 mL toluene at 20 °C and 0.50 g of $CrCl_2$ (THF) was added. The reaction mixture was stirred at 20 °C for 20 h. Hexachloroethane (0.50 g) was added and the mixture was stirred for another 0.5 h. The solvent was removed under vacuum and the crude product was dissolved in CH_2Cl_2 for further purification by column chromatography (column material: Silica 80 A; load 1 g crude product per 200 mL silica). After chromatography a deep violet solution was obtained. After removal of the CH_2Cl_2 under vacuum the residue was stirred in *n*-pentane to obtain the product as a crystalline powder; yield: 0.81 g (37%).

Catalytic Experiments

A Schlenk tube was charged with 0.05 mmol $[(R_5TAC)CrCl_3]$ and 10 mL of toluene. The complex dissolved partly under gentle heating forming a violet colored solution. This reaction mixture was cooled to 20 °C and 10 mL of the 1-olefin and 0.5 mL of cyclohexane as internal standard were added. The mixture was cooled to -50 °C and 5 mmol of MAO or Co-MAO were added, respectively. Then the reaction was allowed to reach 0 °C and this temperature was maintained with a cryostat. To analyze a sample after a certain reaction time, 0.5 mL of the reaction mixture were reacted with 0.5 mL of an aqueous HCl solution (2 M) at room temperature. After centrifugation, the aqueous layer was removed and the organic layer was dried with Na_2SO_4 . The organic layer was then analyzed by gas chromatography using a Siemens Sichromat machine with a 25 m HP Ultra column (temperature program: 0 min iso, 12 °C/min, 50 – 280 °C; evaporator temperature: 300 °C; carrier gas: 2.0 bar H_2).

Viscosity and VI Determination

Isolation of pure trimer oligomers was carried out by removing all C_{10} or C_{12} monomers under vacuum from the isolated organic layer (see above). All samples were hydrogenated (Pd on carbon; 50 bar H_2 ; 25 °C; 16 h) prior to the viscosity determination. All viscosity measurements and the VI determination was carried out at bp/Sunbury, UK according to ISO 2909.

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