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Rare-Earth Catalysts for Carbon–Carbon Linkages of Olefins: Cyclic Oligomerization of Ethylene

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A novel cyclo-oligomerization of ethene to alkylcyclopropanes, alkylcyclopentanes, and alkylcyclohexanes using a Ziegler–Natta type catalyst consisting of rare earth salts such as YCl_3, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $GdCl_3$, $HoCl_3$, $ErCl_3$, $YbCl_3$, $LuCl_3$ combined with $EtAlCl_2$ is described. The addition of carbon monoxide or isonitriles is essential. The C_6-oligomers consist of *n*-propylcyclopropane and methylcyclopentane. The C_8-oligomers include *n*-pentylcyclopropane, *n*-propylcyclopentane, 1,1-methylethylcyclopentane, and ethylcyclohexane. The C_{10}-oligomers embrace *n*-heptylcyclopropane, *n*-pentylcyclopentane, 1-1-methylbutylcyclopentane, 1,1-ethylpropylcyclopentane, and *n*-butylcyclohexane. When the reaction is carried out with rare earth salts and Et_2AlCl or Et_3Al, only open-chain oligomers are obtained. There is no significant influence observed on product selectivity using other rare earth salts. Only the activity is affected. To understand the products formed a metallacycloalkane mechanism is proposed.

INTRODUCTION

Numerous catalysts are known to oligomerize olefins. Two patterns of C–C linkage can be distinguished: open-chain and cyclic oligomerization. For instance, butadiene can be converted catalytically to open-chain oligomers such as methylheptatrienes or octatrienes, or to cyclic ones such as divinylcyclobutanes, vinylcyclohexene, cyclo-octadienes and cyclo-octatrienes (*1*). Also mono-olefins have been successfully oligomerized to open-chain products and many industrial processes emerged, e.g., SHOP-process (*2*) and Dimersol-process (*3*). However, cases of cyclic oligomerizations of mono-olefins are rather rare. Binger *et al.* described the cyclo-oligomerization of highly strained olefins (*4*); Grubbs and Miyashita reported the formation of cyclobutane from ethylene (*5*); Cannell put forward the codimerization of butadiene and ethylene yielding vinylcyclobutane (*6*). In this connection, the trimerization of ethylene to hexene-1 via a proposed chromacycloheptane complex (*7*, *8*) is noteworthy.

In this paper we present our work on the novel cyclo-oligomerization of ethylene applying rare-earth catalysts. The linear oligomerization of ethylene by rare-earth catalysts has been reported already (*9*).

EXPERIMENTAL

All operations were performed in an atmosphere of purified argon. All solvents were dried by proper methods and distilled before use. Ethylene (99.5%) was purified by passing through a dry column filled with $Na(AlEt_4)$. Carbon monoxide (BASF) was directly used as provided. Anhydrous ytterbium chloride ($YbCl_3$ 99.9%) was commercially available from Alfa. The dicyclopentadienyl–ytterbium chloride complex was synthesized according to the literature (*10*). The anhydrous lanthanide chlorides (usually 99.9%) were bought from Alfa or synthesized. The various alkylaluminium com-

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pounds used were commercially available from either Aldrich or Fluka.

The general procedure for the preparation of the catalysts for the ethylene oligomerization, exemplified here for $YbCl_3$, was as follows. Into a suspension of $YbCl_3$ in *n*-heptane the calculated amount of alkylaluminium was added drop-wise under stirring at room temperature. After stirring for 1 h, the catalyst suspension was transferred into a 75-ml steel autoclave equipped with a magnetic stirrer. Ethylene (usually about 40 bar at room temperature) and carbon monoxide (pressured up from 40 bar ethylene to 45 bar) were added. The reaction was conducted in an oil bath at selected temperatures. When the reactions were carried out at 120°C the highest pressure reached was about 80–90 bar. At the end of the reaction a gas sample was taken for GC analysis. The catalyst was destroyed with dilute HCl. The organic phase was washed with water, neutralized with Na_2CO_3, and finally dried over Na_2SO_4 and analyzed by GC.

The GC analyses of the oligomers were performed on a Sichromat 1 gas chromatograph using SE 54 or Pona HP as columns. The isolation of the oligomers by preparative GC was performed on a Hupe APG 402 chromatograph using a 16 m × 2 cm column filled with 20% DC 200 on Kieselgur.

Spectroscopic characterizations. GC–MS: GC, Varian 3700; MS, Varian MAT 112 S, 70 eV ionization energy. ^1H NMR: Varian EM 390, 90 MHz, standard TMS. ^{13}C NMR: Bruker 200 MHz, standard $CDCl_3$.

Characterization of compounds **1–11**. The spectral data for **2, 6,** and **11** are identical with those of authentic samples. The compounds **1, 3, 4, 5, 7, 8, 9,** and **10** were isolated by preparative GC chromatography and characterized by IR, ^1H-, and ^{13}C NMR.

RESULTS AND DISCUSSION

As we have reported previously in a short communication (*11*) the reaction of mixtures of ethylene and carbon monoxide with the Ziegler–Natta catalyst $YbCl_3/AlEtCl_2$ yielded cyclic oligomers. In the absence of

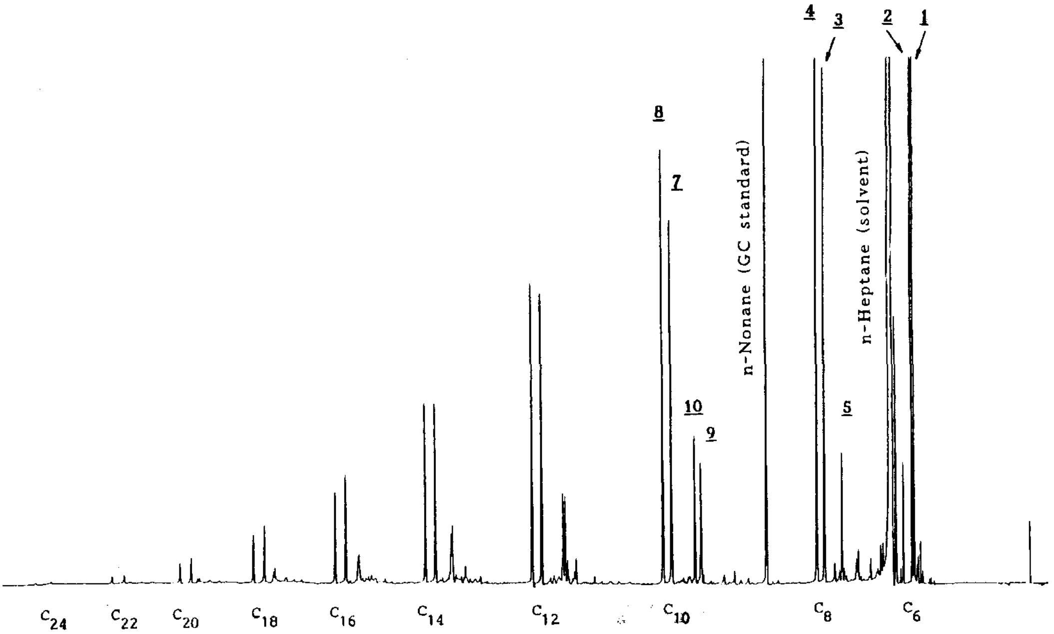
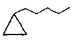
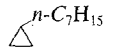
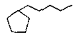
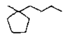
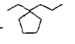
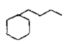


FIG. 1. Gas chromatogram for cyclic oligomers.

TABLE 1

Cyclo-oligomerization of Ethylene by $YbCl_3/AlEtCl_2$

Oligomers (%)			Structure		5 (%)	40 (%)
Al/Yb	5	40				
C_4	0.2	0.1	Butenes			
C_6	21.0	3.2		**(1)**	44	6
				**(2)**	54	91
					98	97
C_8	19.9	10.8		**(3)**	39	4
				**(4)**	46	35
				**(5)**	9	40
				**(6)**	0	14
					94	89
C_{10}	16.8	10.0		**(7)**	33	6
				**(8)**	35	33
				**(9)**	14	19
				**(10)**	14	17
				**(11)**	0	11
C_{12}^+	42.1	75.8			96	86

Note. $YbCl_3$: ca. 0.15 mmol, $C_2H_4/CO = 8$, 120°C, 15 h, 15 ml *n*-heptane.

CO only open-chain oligomers are formed (*9*). A typical gaschromatogram is shown in Fig. 1.

The C_6-oligomers (21%) consisted of *n*-propylcyclopropane **1** and methylcyclopentane **2**. The C_8-oligomers (20%) included *n*-pentylcyclopropane **3**, *n*-propylcyclopentane **4**, and 1,1-methylethylcyclopentane **5**. The C_{10}-oligomers (17%) were characterized as *n*-heptylcyclopropane **7**, *n*-pentylcyclopentane **8**, 1,1-methylbutylcyclopentane **9**, and 1,1-ethylpropylcyclopentane **10**. The isolated and characterized C_4–C_{10}-oligomers amounted to about 56%. The remaining C_{10}^+-oligomers were not characterized due to analytical problems in product separation. However, as is obvious from Fig. 1 the C_{10}^+-oligomers exhibit a similar pattern and it can be assumed that similar structures prevail.

Interestingly, when the ratio Al/Yb is altered from 5 to 40 the product composition changes (Table 1).

At low Al/Yb ratios such as 5 only cyclopropane and cyclopentane derivatives are formed. However, at higher Al/Yb ratios, for instance 40, new products were found which consisted in the C_8-range of **6** ethylcyclohexane and in the C_{10}-range of **11** *n*-butylcyclohexane. If the Al/Yb ratio was 60 **6** amounted to 51% of all C_8-isomers and **11** to 33% of all C_{10}-isomers. If the reaction is carried out with only $EtAlCl_2/CO$ no cyclic products are obtained.

It can be assumed that the cyclohexane derivatives are formed from the cyclopen-

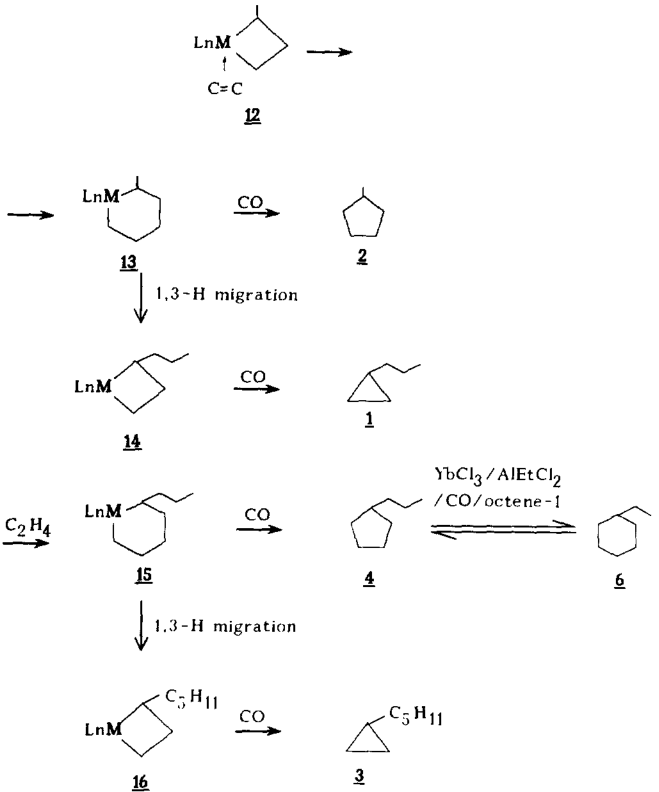


FIG. 2. Mechanism for cyclic oligomer formation.

tane oligomers via isomerization. Such isomerizations catalyzed by Lewis acids like aluminium halides are known from the literature (*12, 13*). Indeed, in a separate experiment *n*-propylcyclopentane **3** could be isomerized by $YbCl_3/AlEtCl_2$ to ethylcyclohexane **6**. Interestingly, when the reaction of ethylene with $YbCl_3/Et_2AlCl$ is carried out with $YbCl_3/EtAlCl_2$ or $YbCl_3/AlEt_3$ only open-chain oligomers are obtained. Furthermore, the addition of CO reduced the activity drastically.

The activity of the cyclo-oligomerization also depends on the reaction temperature applied; at 100°C the turnover numbers (TON) amounted to 77, at 120°C the TON reached 900, and at 140°C the TON was 530. Increasing the temperature yielded cyclohexane derivatives.

The key to changing the ethylene oligomerization from open-chain products to cyclic ones is the addition of carbon monoxide. Carbon monoxide functions as a ligand because it is not incorporated into the products formed. It can be speculated that CO or isonitrile coordinate to the metal thus favouring reductive elimination of the carbon chains as elucidated in Fig. 2. To investigate the impact of the ethylene/CO ratio various experiments were carried out (Table 2).

The selectivity to the products **1–11** changed only slightly. However, the activity was altered significantly. At ethylene/CO ratios above 20 the activity decreased. At ratios above 30 mainly polymers were formed.

Isonitriles possessing coordinating properties similar to those of carbon monoxide were also applied instead of CO. Indeed, the products obtained with cyclohexylisonitrile showed similar selectivities to the cyclic oligomers as obtained with CO. The activity with TON of 896 is also comparable to that of using carbon monoxide [$YbCl_3$ = 0.15

TABLE 2

Impact of Changing the Ratio of C_2H_4/CO

C_2H_4/CO	1.39	4.16	8.33	14.0	18.7	26.8	34.9	60.5
C_2H_4 (mmol)	130	217	357	335	340	287	311	303
CO (mmol)	93.5	52.5	42.9	23.9	18.2	10.7	8.9	5.0
Conversion of C_2H_4 (%)	94.0	95.4	93.0	86.4	96.8	30.0	14.8[a]	11.0[b]

Note. $YbCl_3$: ca. 0.15 mmol, Al/Yb = 40, 120°C, 15 h, 15 ml *n*-heptane.

[a] 35% polyethylene.

[b] 80% polyethylene.

mmol, $AlEtCl_2/YbCl_3 = 40$, cyclohexylnitrile 2,7 mmol, *n*-heptane 15 ml, 15 h 246 mmol ethylene, 150°C].

As is obvious from Fig. 1, the selectivity to the numerous oligomers is bewildering. To transform this new cyclic oligomerization to a reaction of industrial interest, better selectivity is needed. One approach is based on changes in the anionic ligand field. For this investigation $Yb(acac)_3$, $Yb(naphthenate)_3$, and Cp_2YbCl were included. The selectivity was not altered; only differences in activity were observed. The question arises whether this cyclic oligomerization of ethylene is characteristic for the rare-earth ytterbium or whether other lanthanides can be used thus altering the product selectivity? Table 3 summarizes the use of a variety of lanthanides.

TABLE 3

Cyclo-oligomerization of Ethylene by Different Lanthanide Compounds

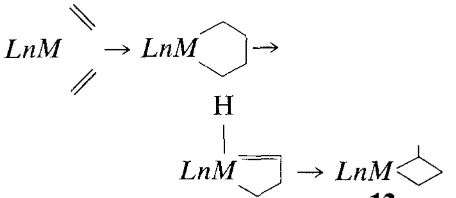
Lanthanide	Selectivity	Activity (TON)
YCl_3	Similar to that of $YbCl_3$	690
$LaCl_3$		175
$CeCl_3$		87
$PrCl_3$		47
$NdCl_3$		69
$SmCl_3$		484
$GdCl_3$		180
$HoCl_3$		171
$ErCl_3$		636
$YbCl_3$		890
$LuCl_3$		230
$Nd(acac)_3 \cdot H_2O$		50
$Sm(acac)_3$		280

Note. TON = mol C_2H_4/mol *M* (*M* = rare-earth metal); temp. 130–150°C; C_2H_4:CO = 6–8; 15–20 h, 0.15 mmol lanthanide, $AlEtCl_2/M$ = 40, 15 ml *n*-heptane.

The product selectivity is very similar to that obtained with $YbCl_3/AlEtCl_2$. However, the activity is different.

Reaction mechanism. In general, two different mechanisms are discussed in oligomerization reactions: a hydride mechanism and a mechanism based on cyclic intermediates (*14*). The products obtained can be understood by advancing a metallacycloalkane mechanism as shown in Fig. 2.

The key intermediate is complex **12,** which can be formed via Eq. (1)



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(1)

Such a reaction is known for rhenium (*15*), tantalum (*16*), and titanium (*17*). It can be speculated that coordination of CO or isonitrile favors the formation of **12** by exhibiting its ligand properties. The unique role of CO (isonitrile) finds a precedent in work reported by Fischer and Dötz (*18*). When pentacarbonyl[methoxy(phenyl)carbon]chromium is heated in the presence of vinyl ether the product of the metathesis is observed. However, upon addition of CO the cyclopropanation product is produced.

Complex **12** inserts ethylene yielding the metallacyclohexane derivative **13,** from which **2** can be obtained via reductive elimination initiated by the ligand CO or isonitrile. Via a 1,3-hydrogen shift **13** can be converted to **14,** from which **1** results by reductive elimination. It is also possible that **14** inserts a further molecule of ethylene thus yielding **15,** from which **4** and **6** can be derived. A 1,3-hydrogen shift converts **15** into **16,** from which **3** is formed.

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