Catalytic ring expansion, contraction, and metathesis-polymerization of cycloalkanes†‡

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Tandem dehydrogenation–olefin-metathesis catalyst systems, comprising a pincer-ligated iridium-based alkane dehydrogenation catalyst and a molybdenum-based olefin-metathesis catalyst, are reported to effect the metathesis-cyclooligomerization of cyclooctane and cyclodecane to give cycloalkanes with various carbon numbers, predominantly multiples of the substrate carbon number, and polymers.

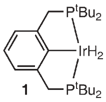
The direct use of alkanes as feedstocks and precursors, in lieu of the corresponding unsaturated species, offers tremendous advantages in terms of energy and cost savings in the synthesis of organic molecules ranging from bulk to fine chemicals. The development of efficient systems for the selective catalytic transformation of unactivated carbon–hydrogen bonds is, accordingly, a subject of intense interest.[1]

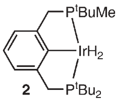
We recently reported a strategy for the catalytic metathesis of *n*-alkanes (eqn 1) which operates *via* a tandem combination[2] of catalytic alkane dehydrogenation and olefin metathesis,[3] and is, unlike other reported catalysts for alkane metathesis,[4] effective for both short and long alkane chain lengths.

$$\begin{aligned} &H_3C(CH_2)_nCH_3 + H_3C(CH_2)_mCH_3 \rightarrow \\ &H_3C(CH_2)_xCH_3 + H_3C(CH_2)_{m+n-x}CH_3 \end{aligned} \qquad (1)$$

The success of this approach with *n*-alkanes suggested the possibility of catalyzing reactions of cycloalkanes analogous to those known for cycloolefins. Most notably, ring-opening metathesis polymerization (ROMP)[5–7] of cycloolefins affords an important route to speciality polymers. In some cases, metathesis catalysts have also been shown to convert cycloolefins to larger rings, albeit typically at high dilution of the substrate and with limited yields.[8–13] Metathesis of cycloalkanes offers the prospect of facile synthesis of large saturated rings which, upon partial oxidation, are important building blocks for pharmaceutical intermediates, fragrances, corrosion inhibitors and polymers.[14] For example, global cyclododecane production exceeds 4 × 10^4 tons per year.[15,16]

Cyclooctane (COA) is a commonly used substrate in studies of alkane dehydrogenation,[17,18] while cyclooctene (COE) is a commonly used monomer for ROMP. Thus COA seemed an ideal starting point for the investigation of catalytic cycloalkane metathesis based on tandem dehydrogenation–olefin-metathesis. As in the case of the *n*-alkane metathesis system, the catalysts used for dehydrogenation were pincer-ligated iridium complexes, **1–3**.[18–23] To catalyze olefin metathesis, we used Schrock's molybdenum-based catalyst, **4**.[24,25]


1
(^{tBu4}PCP)IrH$_2$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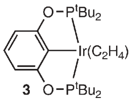
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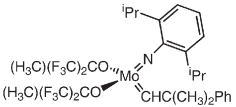
(^{tBu4}POCOP)Ir(C$_2$H$_4$)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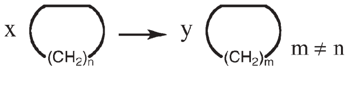
In a typical experiment, ampoules containing a solution of **1** (10 mM), **4** (6.5 mM) and the hydrogen acceptor *t*-butylethylene (TBE; 20 mM) in neat cycloalkane were sealed under vacuum and heated in parallel at 125 °C. Each ampoule was then allowed to cool to room temperature; as it did so, the liquid solution turned gel-like. The mixture was washed several times with toluene and the liquid fractions were then combined. The resulting solutions were analyzed by gas chromatography (GC) with both FID and MS detection.

GC and GC-MS of the toluene-soluble materials showed a distribution of cycloalkane products ranging from C_6H_{12} to $C_{40}H_{80}$, accounting for the transformation of as much as 37% of the COA initially present (Table 1). No non-cycloalkane products were detected, other than 2,2-dimethylbutane (from the hydrogenation of TBE). To our knowledge, there are no reported precedents for this type of transformation, *i.e.*, cycloalkane metathesis (eqn 2).



(2)

As Table 1 shows, the cycloalkane products are predominantly of the formula $C_{8n}H_{16n}$, where n = 2–5. Formation of these products can be readily explained according to the tandem catalytic cycle depicted in Scheme 1.

The second sub-cycle of Scheme 1 (right side) depicts the ring-opening–ring-closing oligomerization of cyclooctene. Cyclooligomerization of cycloalkenes by the olefin-metathesis catalysts WCl_6–$EtAlCl_2$[8] or Re_2O_7–Al_2O_3[9,10] is precedented. In particular, dimerization and trimerization of cyclooctene, to give

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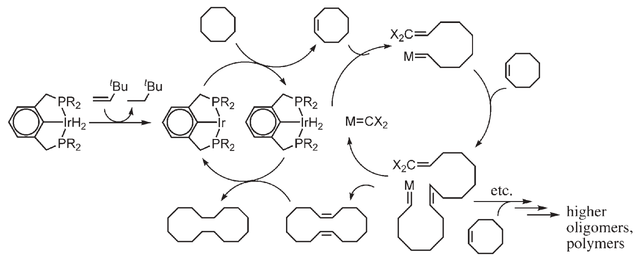
† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Experimental details and procedures, full tables with product distribution for carbon number ⩽ 40, GPC traces. See DOI: 10.1039/b712197k

Table 1 Results of metathesis of COA by catalyst **4** and one of catalysts **1**, **2**, or **3** at 125 °C. Distribution of products (weight %)[a,b]

			Cycloalkanes (% by weight)												
Cat.	TBE/mM	Time/h	C_6	C_7	C_8	C_{15}	C_{16}	C_{17}	C_{24}	C_{32}	C_{33}	C_{40}	Sum $C_{6–40}$ prod.	Insol. %	% Conv. C_8
1[c]	10	24	0.0	1.3	**79**	0.0	0.7	0.3	0.3	0.2	0.1	0.1	3.8	7.8	21
1[c]	10	72	0.2	2.7	**61**	0.1	1.9	0.6	0.7	0.4	0.2	0.2	7.8	16	39
1[c]	20	24	0.1	2.7	**73**	0.1	0.7	0.4	0.3	0.1	0.1	0.1	5.3	11	27
1[c]	20	72	0.3	4.0	**47**	0.1	3.2	0.7	1.2	0.5	0.2	0.3	11.5	29	53
1[c]	100	24	0.3	5.3	**45**	0.1	0.7	0.4	0.3	0.1	0.1	0.1	8.2	32	55
1[c]	100	72	0.5	5.6	**43**	0.1	1.3	0.4	0.6	0.2	0.1	0.1	9.9	33	57
2[d]	20	6	0.1	0.2	**41**	0.0	14	0.3	9.4	4.6	0.1	2.2	32	4.0	59
2[d]	20	12	0.1	0.3	**20**	0.0	14	0.3	10	5.6	0.2	2.7	34	10	80
3[e]	20	24	0.0	0.3	**42**	0.0	15	0.2	10	4.0	0.1	1.2	37	5.6	58

[a] Heating beyond times given did not afford significant additional product. Other ring sizes, formed in lesser amounts, are described in the ESI. [b] Insol. = material insoluble in toluene at ambient temperature. [c] C_8H_{16} (0.75 mL, 625 mg); **1** (4.4 mg; 10 mM); **4** (3.7 mg; 6.5 mM). [d] C_8H_{16} (0.75 mL, 625 mg); **2** (4.2 mg; 10 mM); **4** (3.7 mg; 6.5 mM). [e] C_8H_{16} (1.5 mL, 1.25 g); **3** (14.0 mg; 15 mM); **4** (11.5 mg; 10 mM).

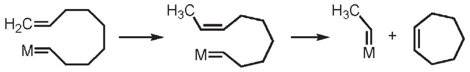


Scheme 1 Proposed mechanism of cycloalkane oligomerization.

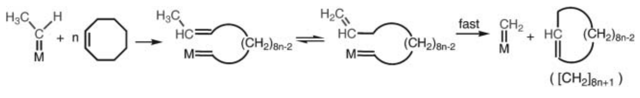
cyclo-$C_{16}H_{32}$ and cyclo-$C_{24}H_{48}$, respectively, has been reported,[8] in addition to analogous dimerizations of cycloheptene, cyclononene, and cyclodecene.[9,10] However, these ring expansions proceed efficiently only at very low concentrations of the cycloolefin reagent,[8–10] whereas cycloalkane metathesis can be conducted in the neat cycloalkane due to the low steady-state concentration of the cycloolefin created in the first sub-cycle of Scheme 1 (left side).

The transformation of significant quantities of COA to give cycloalkanes with carbon numbers that are *not* multiples of 8 seemed at first to be an even more surprising result. However, pincer–iridium catalysts,[19] as well as **4**,[26] readily catalyze olefin isomerization (double-bond migration) under the conditions of these experiments. If the ring-opened intermediate (Scheme 1) isomerizes to an internal olefin, subsequent ring-closing would give smaller, less strained rings (shown in eqn 3 for cycloheptene formation).

The ethylidene complex formed in eqn 3 could react with cyclooctene to give ring-opened complexes with the double-bond at the β position (Scheme 2). Although subsequent isomerization from the β- to α-olefinic intermediate would be endergonic, the resulting α-olefinic species would close more rapidly;[27] thus the formation of substantial quantities of $[CH_2]_{(8n+1)}$ can also be explained, as illustrated in Scheme 2.



(3)



Scheme 2 Formation of $(CH_2)_{8n+1}$ cycloalkanes.

As seen in Table 1, the combination of catalysts **2** and **4** gives significantly greater yields of ring-expanded products, in shorter reaction times, than does catalyst combination **1**–**4**. Furthermore, catalyst combinations **2**–**4** and **3**–**4** offer significantly higher selectivity for $C_{8n}H_{16n}$ products, with very little cycloheptane formed and relatively smaller quantities of cycloalkanes with carbon numbers that are not multiples of 8. These results may suggest that the rate of double-bond isomerization by **2** and **3** is lower than that by **1**. Future mechanistic studies will address this issue in more detail.

The total mass of insoluble and $C_{\leqslant 40}$ products (and unreacted COA) accounted, in some cases, for significantly less than 100% of the initial COA (see Table 1). The remaining material appears to be soluble products that are not sufficiently volatile to be detected by GC or GC-MS. This conclusion is supported by gel permeation chromatographic (GPC) analysis of the toluene–cycloalkane solution, which showed several peaks corresponding to molecular weights greater than that of $C_{40}H_{80}$ (>560).

The *insoluble* material obtained from the reactions was analyzed separately by GPC (135 °C). The GPC trace of the material obtained from the reaction catalyzed by **1**–**4** was found to be distinctly bimodal. The minor component is a mixture of oligomers, which are likely less soluble cycloalkanes with carbon numbers > 40 (maximum at $M_w = 965$). The major component comprises higher molecular weight polyethylene with $M_w = 49\,600$ and $M_n = 29\,700$ (PDI = 1.67; see ESI‡).[28] The formation of polyethylene in the reaction of COA catalyzed by **1**–**4** is presumably the result of ring-opening metathesis polymerization (ROMP) of cyclooctene, coupled with rehydrogenation of the growing chain. Accordingly, the formation of insoluble product is favored by higher initial concentrations of TBE (see Table 1), which presumably result in higher steady-state concentrations of COE.

It is possible that some or all of the polyethylene is cyclic. Cyclic polyethylene has been prepared previously by cyclopolymerization of COE using a macrocyclic Ru carbene complex, followed by a separate hydrogenation step.[29]

In contrast with the products of the **1**–**4**-catalyzed reaction, GPC of the insoluble material obtained from the tandem reaction of COA with **3**–**4** revealed only oligomer ($M_w = 1086$, $M_n = 774$, PDI = 1.4), and no higher molecular-weight polymer. The insoluble material from the reaction catalyzed by **2**–**4** lies between these extremes, (mostly oligomer, but with significant amounts of

Table 2 Results of metathesis of CDA by **4** and **1** or **2** at 125 °C.[a,b] Distribution of products (weight %)

		Cycloalkanes (% by weight)										
Cat.	Time/h	C_{10}	C_{19}	C_{20}	C_{21}	C_{29}	C_{30}	C_{31}	C_{40}	Sum C_{6-40}	Insol.	% Conv. C_{10}
1	48	**58**	0.4	1.7	0.4	0.1	0.4	0.1	0.1	5.7	18	42
1	96	**31**	0.6	3.7	0.6	0.2	0.9	0.2	0.4	9.2	37	69
1	144	**7.6**	0.8	8.5	0.9	0.5	3.0	0.6	1.1	19	53	92
2	6	**83**	0.1	2.0	0.1	0.0	0.3	0.0	0.1	4.6	8.7	17
2	12	**79**	0.1	3.2	0.1	0.0	0.3	0.0	0.1	5.7	11	21

[a] See Table 1 footnotes. [b] $C_{10}H_{20}$ (0.5 mL; 435 mg); TBE (1.3 μL; 20 mM); **1** (3.0 mg; 10 mM) or **2** (2.8 mg; 10 mM) and **4** (2.5 mg; 6.5 mM).

polymer). Thus the yield of polymeric (possibly cyclic) products, relative to ring-expanded cycloalkanes, varies greatly with the nature of the catalyst. We suspect that the same factor that favors formation of cycloheptane and other non-C_{8n} species by catalyst **1**, *i.e.*, a greater rate of α- to β-double-bond isomerization, also results in a decreased rate of ring closure by the growing chain due to the much lower reactivity of internal double-bonds; polymerization is thereby favored relative to cyclooligomerization.

Cyclodecane (CDA) was also found to undergo metathesis-oligomerization catalyzed by **4** and either **1** or **2** (Table 2). The major cyclic products have the formula $C_{10n}H_{20n}$; the yields decrease with increasing values of *n*, as is the case with COA. Unlike with COA, no ring contraction products (carbon number less than 10) were observed; formation of cyclononane would not afford the same reduction in strain as is achieved in the formation of cycloheptane from COA. However, a somewhat greater quantity of "non-integral" cyclooligomers (*e.g.* $C_{19}H_{38}$ or $C_{29}H_{58}$, but not cyclononane) is formed. The yields of polymer, and oligomers with carbon number > 40, are comparable to those obtained from COA.

Cyclohexane and cycloheptane were also screened for metathesis. Under the same reaction conditions as used for COA or CDA, no reaction was observed with these relatively unstrained cycloalkanes.

In summary, tandem dehydrogenation–olefin-metathesis catalyst systems effect the metathesis-cyclooligomerization of COA and CDA to give cycloalkanes with different carbon numbers, predominantly multiples of the substrate carbon number. Dimers are the major product, with successively decreasing amounts of higher cyclooligomers formed. In addition, polymerization of the cycloalkanes can occur. Both cyclooligomerization (metathesis) and polymerization of cycloalkanes are unprecedented. Future work will focus on (i) controlling and understanding selectivity with respect to both the polymer : cycloalkane ratios as well as the M_w's of either type of product, and (ii) extending these reactions to functionalized saturated molecules in an effort to make the corresponding functionalized macrocycles or polymers.

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