Supplementary Material (ESI) for Chemical Communications

Catalytic Ring Expansion, Contraction, and Metathesis-Polymerization of Cycloalkanes

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Supporting Information

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I. Experimental Section

MATERIALS AND METHODS

General Considerations

All manipulations were carried out using standard Schlenk and glove box techniques. Cyclooctane (COA, >99%), cyclohexane, cycloheptane, *tert*-butylethylene (TBE; 3,3-dimethyl-1-butene), *p*-xylene and mesitylene were purchased from Aldrich. Cyclodecane (CDA, >99%) was purchased from Fluka. All the compounds were degassed via several freeze-pump-thaw cycles, stirred and dried over Na-K, collected and then stored under argon in a glove box. (^{tBu4}PCP)IrH$_2$ (**1**),[1,2] (^{tBu3Me}PCP)IrH$_2$ (**2**),[3] and (^{tBu4}POCOP)Ir(C$_2$H$_4$) (**3**)[4] were synthesized according to literature procedures. Mo(=CHCMe$_2$Ph)(=NC$_6$H$_4{}^{i}$Pr$_2$)[OC(Me)(CF$_3$)$_2$]$_2$ (**4**) was purchased from Strem and used as received. GC-MS measurements were performed with a HP 5890 Series II Plus instrument fitted with a Varian CP-Sil 5 CB capillary column (15 m x 0.25 mm ID x 0.25 μm film thickness).

High temperature gel permeation chromatography (GPC) analyses of reactions of COA catalyzed by **1** or **2** were performed with a Waters Alliance GPCV 2000 GPC equipped with a Waters DRI detector and viscometer. The column set (four Waters HT 6E and one Waters HT2) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt. % di-tert-butylhydroxytoluene (BHT) at 1.0 mL/min at 140 °C. Data were calibrated using monomodal polystyrene standards (from Polymer Standards Service). Polymers were usually placed in a 140 °C oven for 24 h prior to molecular weight measurements.

Polyethylene samples from the reactions using **3** were hot-filtered using a PL-SP 260VS Sample Preparation System. 20-25 mg of each sample was weighed in disposable vials to which 15 g o-dichlorobenzene was added. The suspensions were then heated at 140 °C for 1 h with agitation. The samples were then transferred via a heated filter pipette, equipped with 0.5-μm stainless steel filters, to 2-mL GPC autosampler vials, which were then crimped and transferred to the GPC autosampler of a Polymer Laboratories Pl-GPC-200. Samples were characterized at 135 °C. A refractive index detector was used and calibrated using Polymer Labs polystyrene standards.

GC analyses (FID detection) were performed on a Thermo Electron Corporation Focus GC instrument fitted with an Agilent HP-1 100% methyl silicone gum column: 25m length x 0.2 mm ID x 0.5 μm film thickness using the following GC method:

GC Method
Detector: FID
Starting temperature: 40 °C
Time at starting temp: 1.4 min
Ramp1: 20 °C/min up to 250 °C with hold time = 3 min
Ramp2: 20 °C/min up to 300 °C.
Ending temperature: 300 °C
Flow rate: 1 mL/min (He)
Split ratio: 25
Inlet temperature: 300 °C
Detector temperature: 350 °C

Representative Procedure for Cycloalkane Metathesis Reactions.

In an argon-filled glovebox, **1** ($(({}^{t\mathrm{Bu}4}\mathrm{PCP})\mathrm{IrH}_2$, 12 mg, 0.021 mmol), **4** ($\mathrm{Mo({=}CHCMe_2Ph)({=}NC_6H_4{}^{i}Pr_2)[OC(Me)(CF_3)_2]_2}$, 10 mg, 0.013 mmol) and TBE (5.2 μL, 0.042 mmol) were added to cycloalkane (2 mL) containing *p*-xylene (0.0405 M) as an internal standard). Aliquots of this solution (0.75 mL or 0.5 mL each) were transferred to glass ampoules. The contents were cooled under liquid nitrogen and then sealed under vacuum. These sealed ampoules were heated (in parallel) in a preheated oven at 125 °C.

The reaction mixtures were monitored by GC at various time intervals. An ampoule was brought to room temperature, at which point the red colored solution generally turned viscous and became a gel (in samples subject to prolonged heating, the solution almost solidified when cooled). The seal of the ampoule was then broken and toluene (1-2 mL) was added to the ampoule. The ampoule was covered with a septum and warmed to 90 °C and shaken to dissolve soluble components. The mixture was then cooled to room temperature and centrifuged, and the supernatant was removed. This procedure was repeated several times (all washings were combined) to effect a thorough extraction of soluble material. Accordingly, the final toluene extractions were colorless, indicating that the soluble colored catalysts had been completely extracted.

The toluene extract was analyzed by GC after the addition of mesitylene (10 μL) as an internal standard (in addition to the *p*-xylene added prior to the reaction). Products of carbon number up to 40 were observed by GC; of these, the identity of products of carbon number up to 26 were confirmed by GC/MS.

After washing was completed, the insoluble material was dried under vacuum and then weighed. Both toluene extract and insoluble material were subject to GPC analysis.

II. GC data for cycloalkane metathesis

Table S1. Results of metathesis of COA (625 mg) by catalysts **4** and **1**, **2**, or **3** at 125 °C.[a] Distribution of products (mg).

			mass (mg)														
			cycloalkane products														**% conv. C_8**
entry	**Cat.**	**Time (h)**	**C_6**	**C_7**	**C_8**	**C_{15}**	**C_{16}**	**C_{17}**	**C_{23}**	**C_{24}**	**C_{25}**	**C_{32}**	**C_{33}**	**C_{40}**	**Sum $C_{6,7,9\text{-}40}$**	**insol.**	
1[c]	**1**	24	0.8	17	456	0.4	4.4	2.5	0.5	1.6	0.8	0.7	0.5	0.5	33	70	27
2[c]	**1**	72	1.8	25	294	0.7	20.3	4.4	0.9	7.3	1.7	2.9	1.1	1.7	72	180	53
3[d]	**2**	6	0.5	1.5	254	0.2	88	1.7	0.5	59	1.3	29	0.9	14	198	25	59
4[d]	**2**	12	0.5	2.1	127	0.2	89	1.6	0.5	64	1.4	35	1.1	17	214	63	80

(a) Heating beyond times given did not afford significant additional product. (b) insol. = material insoluble in toluene at ambient temperature. (c) C_8H_{16} (0.75 mL, 625 mg); TBE (1.3 µL; 20 mM); **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, 1250 mg); TBE (1.3 µL; 20 mM); **3** (14.0 mg; 15.2 mM); **4** (11.5 mg; 10 mM). To facilitate comparison with runs in which 0.75 mL COA was used, the values given are one half the actual product masses.

Table S2. Results of metathesis of CDA (435 mg) by **4** and **1** or **2** at 125 °C.[a,b] Distribution of products (mg).

			mass (mg)										% conv. C_{10}
			cycloalkane products									insol.	
entry	Cat.	Time (h)	C_{10}	C_{19}	C_{20}	C_{21}	C_{29}	C_{30}	C_{31}	C_{40}	Sum $C_{6\text{-}9,11\text{-}40}$		
1	**1**	48	254	1.8	7.3	1.7	0.6	1.6	0.6	0.5	25	77	42
2	**1**	96	136	2.6	16	2.4	0.9	3.7	0.9	1.6	40	161	69
3	**1**	144	33	3.6	37	4.0	2.2	13	2.4	4.7	81	230	92
4	**2**	6	362	0.3	8.7	0.3	0	1.3	0.1	0.3	20	38	17
5	**2**	12	345	0.5	14	0.5	0.1	1.5	0.1	0.3	25	46	21

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

III. GPC traces

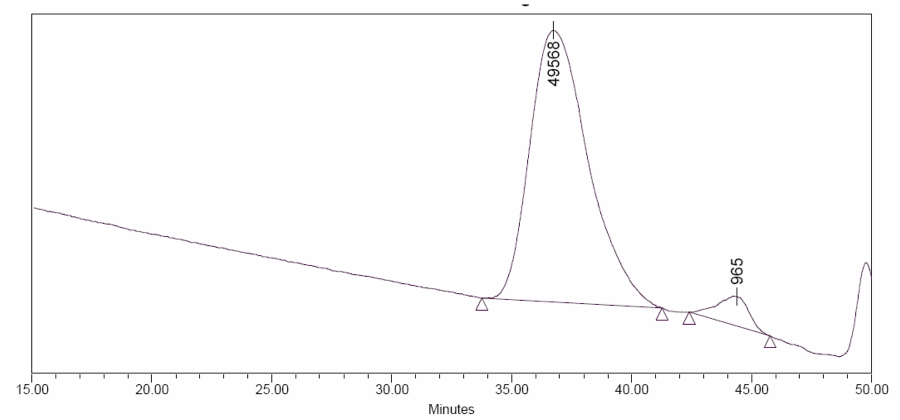

Figure S1. GPC trace of the insoluble fraction obtained from the reaction of COA catalyzed by **1** and **4**. See Table 1 for reaction conditions.

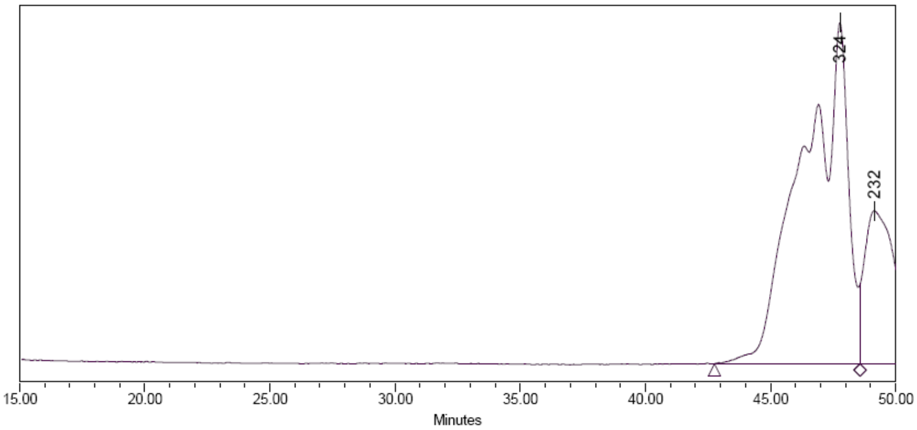

Figure S2. GPC trace of the soluble fraction obtained from the reaction of COA catalyzed by **1** and **4**. See Table 1 for reaction conditions.

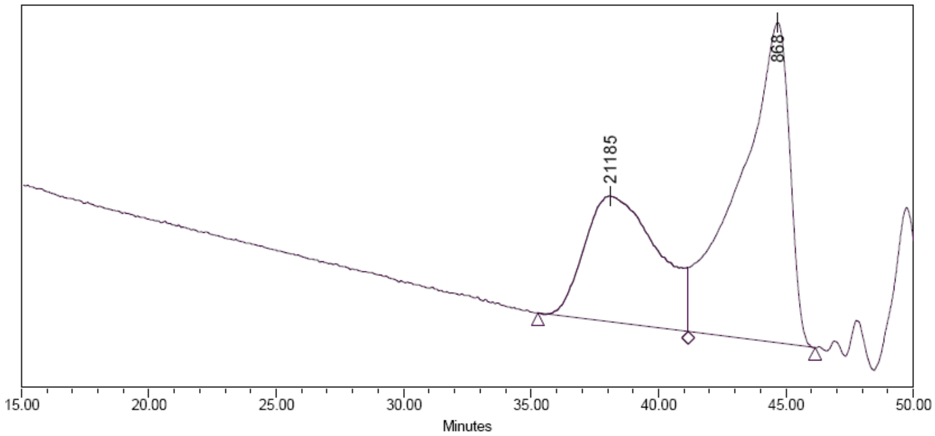

Figure S3. GPC trace of the insoluble fraction obtained from the reaction of COA catalyzed by **2** and **4**. See Table 2 for reaction conditions.

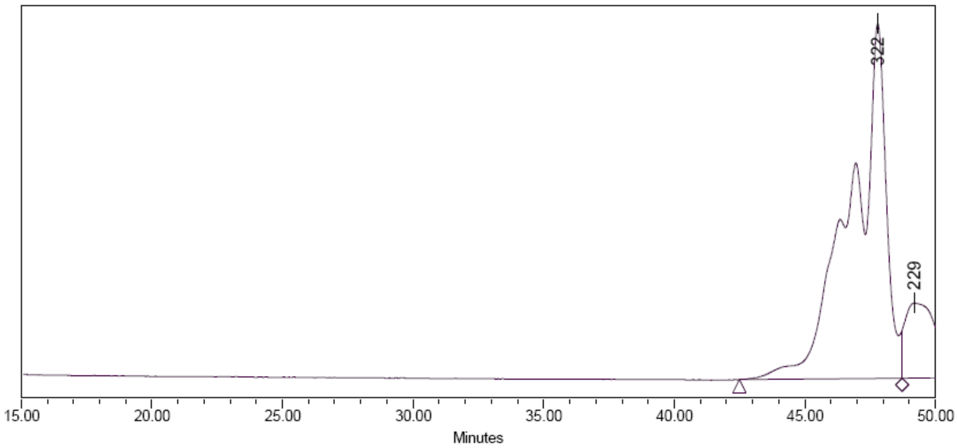

Figure S4. GPC trace of the soluble fraction obtained from the reaction of COA catalyzed by **2** and **4**. See Table 2 for reaction conditions.

IV. References

[1] M. Gupta, M.; C. Hagen, R, J. Flesher, W.C. Kaska, C. M. Jensen, *Chem. Commun.* 1996, 2083.

[2] A. S. Goldman, R. Ghosh, In *Handbook of C-H Transformations - Applications in Organic Synthesis*; Dyker, G., Ed.; Wiley-VCH: New York, 2005, p 616-621.

[3] S. Kundu, S. A. S. Goldman, manuscript in preparation.

[4] (a) I. Göttker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* 2004, **126**, 1804. (b) I. Göttker-Schnetmann, M. Brookhart, *J. Am. Chem. Soc.* 2004, **126**, 9330.