One-pot Synthesis of 1,3-Butadiene and 1,6-Hexandiol Derivatives from Cyclopentadiene (CPD) via Tandem Olefin Metathesis Reactions

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Dedication ((optional))

Abstract: A novel tandem reaction of cyclopentadiene (**CPD**) leading to high value linear chemicals via ruthenium catalyzed ring opening cross metathesis (ROCM) followed by cross metathesis (CM) is reported. The ROCM of cyclopentadiene **(CPD)** with **ethylene** using commercially available 2nd gen. Grubbs metathesis catalysts (**1-G2**) gives 1,3-butadiene (**BD**) and 1,4-pentadiene (**7**) (and 1,4-cyclohexadiene (**12**)) with reasonable yields (up to 24% (**BD**) and 67% (**7**+**12**) at 73% **CPD** conversion) at 1-5 mol% catalyst loading in toluene solution (5 V% **CPD**, 10 bar, RT) in an equilibrium reaction. The ROCM of **CPD** with *cis*-butene diol diacetate (**2**) using 0.01 mol% of 3rd gen. Grubbs (**1-G3**) or 2nd gen. Hoveyda-Grubbs (**1-HG2**) catalysts loading gives hexa-2,4-diene-1,6-diyl diacetate (**8**), which is a precursor of 1,6-hexanediol (an intermediate in polyurethane, polyester and polyol synthesis) and hepta-2,5-diene-1,7-diyl diacetate (**9**) in good yield (up to 68% or TON: 1180). Thus, a convenient and selective synthetic procedure is revealed by ROCM of **CPD** with **ethylene** and **2** leading to **BD** and 1,6-hexanediol precursor, respectively, as key components of commercial intermediates of high-performance materials.

Introduction

Cyclopentadiene (**CPD**) is a volatile, low strained and reactive conjugated cyclic diolefin having minimal commercial value. Nevertheless, it has unique chemical properties among the cycloolefins as its hydrogen atoms undergo facile [1-5]-sigmatropic shift.[1,2] Moreover, **CPD** is an exceptionally acidic hydrocarbon, which can be easily deprotonated giving an aromatic cyclopentadienyl anion.[3] The main reactions of **CPD** includes cycloaddition,[4–9] addition,[10] substitution[11] and oxidation[12] reactions however its consecutive Diels-Alder reaction leading to **CPD** polymers or oligomers are also reported.[13]

The unusual chemical properties and low commercial value of **CPD** have prompted us to investigate its activity in olefin metathesis reactions. In this paper a tandem reaction – ring opening cross metathesis (ROCM) followed by cross metathesis (CM) – of **CPD** leading to value added chemicals such as butadiene (**BD**) or 1,6-hexandiol derivatives is reported.

The petrochemical industry continues to face enormous challenges from product development and diversification, and nowadays also from sustainability. For example, three decades ago the plastic production was based on ethylene, propylene and the aromatic BTX-fractions almost solely. Thus, refineries were optimized for the production of these compounds.[14] C4 and C5 olefin and diene streams or components were considered as low-value intermediates and were typically recycled in steam-crackers in order to increase the yields of the light olefins. Curiously, the price of **BD** became attractively low enough to replace aromatics with **BD** as major feedstock for nylon production until the mid or late 90's.

However, by the time the appropriate technologies and plants were developed by the main nylon producers,[15] the price of **BD** had skyrocketed putting the butadiene-based nylon routes on hold. The exploding demand for **BD** came from the development of engineering plastic and high-performance materials. Thus, **BD** has found major applications in styrene-butadiene rubbers (SBR), polybutadiene rubber (PBR), acrylonitrile butadiene styrene (ABS) resins, styrene-butadiene (SR) latex and others in decreasing importance.[16] Its market is expected to grow further, higher than with the present 5% per year in the coming 5 years. Most of the produced **BD** is obtained by extraction procedures of the C4 streams of naphtha or oil steam-crackers, which contain roughly 5% **BD**.[16] **BD** can also be produced by already proven, although not widely applied technologies via dehydrogenation of butane and/or butenes.[17–23]

Another emerging area is the production of 1,6-hexanediol, which can be used as intermediate in polyurethanes (PUR), acrylates, polyesters (e. g. PET), polyols (for example, in reaction with propylene oxide), coatings and plasticizers represent a large slice of the present plastic slate of the world.[24] The market of 1,6-hexanediol is estimated at USD 730 million in 2016 and is projected to grow over 1 billion USD by 2021.[25] This intermediate is an emerging material, which is not only a high-value building block in the above mentioned commercial polymers, but it can also be used as precursor for adipic acid production via aerobic oxidation using heterogeneous Pt, Au and Pd based catalyst systems.[26]

Despite the fact that many valuable materials and intermediates (such as polyisoprene, butylrubber, styrene-isoprene-butadiene polymers, unsaturated polyesters, norbornene, ethylidene norbornene, EPDM elastomers, other dicyclopentadiene-based plastics etc.) are already made from the C5 streams of naphtha or oil steam-crackers,[27] most of these

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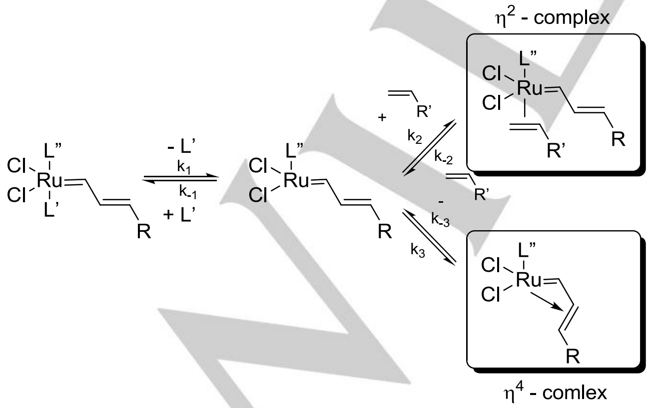
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) fractions are still underutilized and typically re-cracked.[28] By using high severity in present steam-cracker technologies, a 100 Mt/y amount of ethylene production generates 4.1 Mt/y of cyclopentadiene (**CPD**) using naphtha as feedstock.[29–31] In contrast, the global production of one of the most important C5 components, **CPD,** including dicyclopentadiene (**DCPD**) is only 680 kt/y.[32,33]

The commercial impact of organometallics to the petrochemical downstream industry is enormous. Transition-metal-catalyzed olefin metathesis (OM) was first invented for use in the petrochemical industry more than 50 years ago by Phillips Petroleum Co.[34] By now, OM became an indispensable and intrinsic part of the synthetic arsenal that initiated new technological avenues leading to innovative materials, petrochemicals and pharmaceuticals.[35]

Here we report on a very convenient and selective synthetic procedure by using ROCM of **CPD** with **ethylene** and *cis*-but-2-ene-1,4-diyl-diacetate (**2**), leading to **BD** and hexa-2,4-diene-1,6-diyl diacetate (**8**), as key components of commercial intermediates for high-performance materials in enginering plastic. The metathesis of **DCPD** with ruthenium metathesis catalysts is well-known and has been investigated in detail.[36] However, the reported metathesis reactions of **CPD** and other compounds containing conjugated double bonds are rare.[37] This is not surprising as **CPD** is relatively unstable, it can spontaneously dimerize to **DCPD** via Diels-Alder (DA) reaction.[38,39] In addition, the conjugated electron system is expected to reduce activity in metathesis reactions via the formation of less or non-reactive η^4-allylidene(vinylcarbene) species (Scheme 1).[40–42]

Moreover, ruthenium η^4-allylidene systems disposing distorted geometry have already been isolated from enyne metathesis reaction mixtures.[43] It was found that these complexes show very limited catalytic activity. Nevertheless, systematic experimental and theoretical studies of the “cascade” metathesis of conjugated olefins have recently been carried out in our laboratory indicating that the conjugation of the double bonds itself have no significant impact on the overall catalyst performance.



Scheme 1. General scheme of the mechanism of metathesis of conjugated olefins, tentative formation of η2 and η4 - allylidene ruthenium complexes.

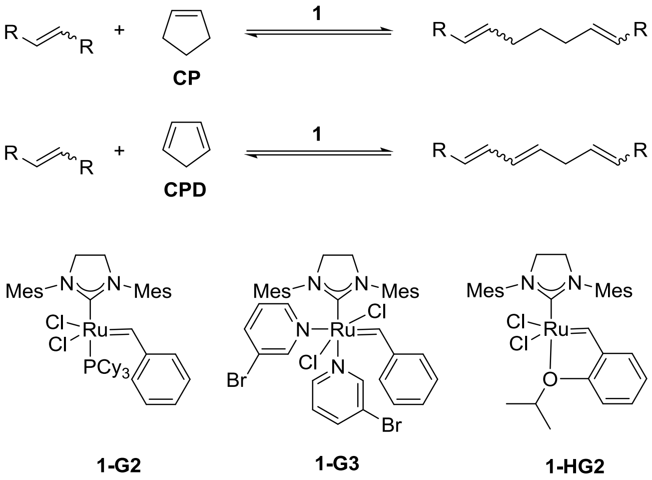
However, the use of cross-coupling agents containing electron withdrawing groups (i.e. like acrylonitrile)[44–46] “shut down” the secondary metathesis step of the cascade reactions via the formation of an electron deficient, less nucleophile conjugated intermediate.[42]

The ring opening metathesis polymerization (ROMP) or ring opening cross-metathesis (ROCM) of cycloolefins is driven by the release of ring strain energies.[47] If the ring strain falls between 3 – 8 kcal/mol, then equilibrium polymerization is expected.[48,49] It has been reported that the ring strain energy of **CPD** is similar to that of cyclopentene (**CP**),[50] whose equilibrium ring opening metathesis polymerization has recently been investigated in our laboratories.[51,52] Considering the similar ring strain energies of **CPD** and **CP** it was assumed that these two compounds should maintain similar thermodynamic properties in ROMP/ROCM reactions (Table 1; ref. A[53]; ref. B[50]). As expected for an equilibrium polymerization (e.g. ROMP of cyclopentene**)** using either Grubbs or $WCl_6/Al(C_2H_5)Cl_2$ catalysts, the monomer equilibrium concentration is not affected by the catalyst activity but the reaction temperature.[54,55]

Despite the relative instability of neat **CPD** at room temperature it was supposed that the DA reaction can be hindered using low temperature and/or diluted solutions.[29] Considering the mediocre ring strain, it was presumed that the ring opening cross-metathesis (ROCM) of **CPD** should be feasible in diluted solution (5 V%) using an excess of electron rich cross-coupling agents (such as ethylene, *cis*-butenediol diacetate (**2**) or *cis*-stilbene (**3**)) and highly active metathesis catalysts systems (**1**) (Scheme 2). As mentioned above, the ring opening metathesis reactions of **CPD** has not been investigated yet in detail, unlike that of its cycloadduct, **DCPD**.[37,56]

Table 1. Ring strain energies of **CP** and **CPD** (E_{str}).

compound	E_{str} (kcal/mol)	
CP	5.47[40]	5.69[37]
CPD	5.98[40]	5.02[37]



Scheme 2. General scheme of ROCM of **CP** and assumed ROCM of **CPD** by using commercially available ruthenium catalysts (**1**).

Results and Discussion

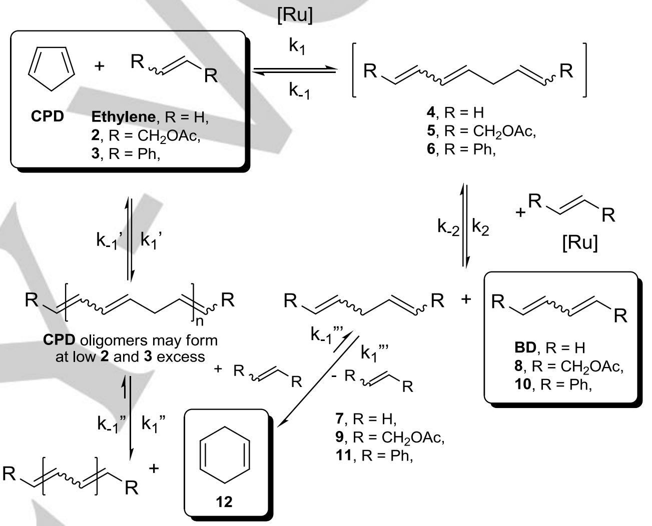
First the feasibility of the ROCM of **CPD** has been investigated with *cis*-stilbene (**3**) at 25 °C. Compound **3** is an ideal choice as a model compound for cross-metathesis (CM) reactions because its reaction with catalysts **1** does not lead to the formation of less active intermediate. Thus, the rate and conversion of the ROCM reaction between **CPD** and **3** is supposedly determined by **CPD** only.

The ROCM investigation of the reaction of **CPD** with eight-fold excess of **3** (four-fold excess per double bond) mixtures in the absence and presence of **1-HG2** catalyst have been carried out at 25 °C in toluene-d_8 solution (5 V%) and monitored by *in-situ* ^{1}H NMR spectroscopy (Figure 1). As expected, relatively fast (r = $7.8 \cdot 10^{-5}$ 1/s) ROCM reaction rate was observed meanwhile there were no DA product formation revealed when the reaction was repeated at the same conditions in the absence of catalyst (Figure S1). The **CPD** conversion was almost 100% based on *in-situ* NMR investigation (Figure 1, 2) and the formations of 1,4-diphenylbuta-1,3-diene (**10**) and 1,5-diphenylpenta-1,4-diene (**11**) were observed in high yields (**10**: 77%, **11**: 80%). Based on the integral areas of the crude, non-hydrogenated reaction mixture 20-80% *Z-E* stereoisomer ratio could be estimated for each product.

The GC-MS investigations of the hydrogenated reaction mixture have shown minor amount of hydrogenated homologs (C6 and C8-C14) of **6**, **10** and **11** with evenly declining integral areas (Figure S4). The presence of homologs can be explained by the inherent self-metathesis of the reaction products. Hypothetically the formation of minor amount of **CPD** oligomers may also be expected giving high molecular weight homologs, which were not detected by the GC-MS.

Stochiometric experiments with **3** revealed the formation of some primary product, (hepta-1,3,6-triene-1,7-diyl)dibenzene, (**6**) however the secondary metathesis products **10**, **11** and their homologs (C6 and C8-C14) were also present in reasonable yield (**10**: 10.6% and **11**: 9.5%, based on GC-MS integral areas). Precipitation was also observed indicating some **CPD** oligomerization reactions.

At extended reaction time however, significant amount of 1,4-cyclohexadiene (**12**) formation (up to 42%) was observed (Figure S2). Hypothetically **12** may form via either the self-metathesis of **CPD** oligomers or **11** (Scheme 3). This observation indicates that the rate of the secondary metathesis step (k_2) should be relatively faster than that of the primary (k_1). Nevertheless, the rate of the formation of **12** (k_1'' or k_1''') is supposedly slow (Scheme 3). Furthermore, according to computational studies the secondary metathesis products (**10** and **11**) have higher thermodynamic stability compared to the primary species (**6**) (Figure 3).



Scheme 3. Conversion of **CPD** via ROCM using commercially available Grubbs catalyst systems (**1**).

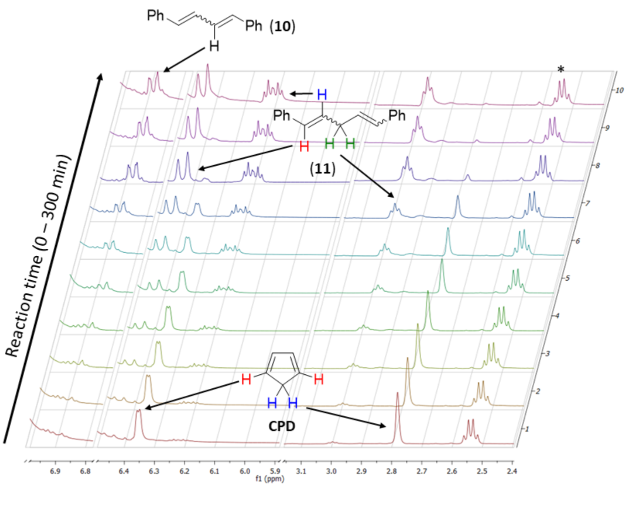


Figure 1. *In-situ* ^{1}H NMR investigation of the ROCM of **CPD** with **3** as model compound. (Toluene-d_8, 5V% (0.543 M), room temperatrure, **1-HG2** 1 mol%, **3** (4.34 M, 8eq). (see full spectra in suppl. mat. Figure S5). *Ethylbenzene, internal standard

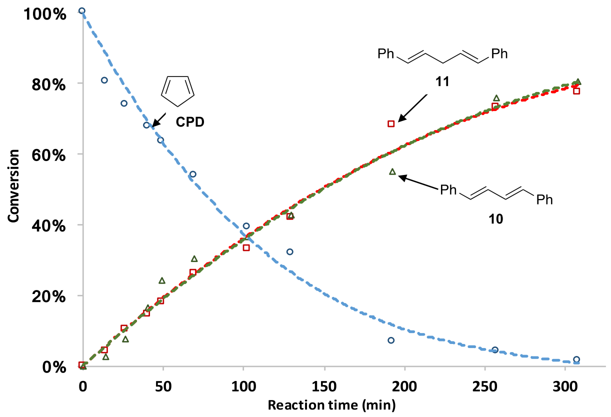


Figure 2. Conversion of **CPD** and the formation of secondary metathesis reaction products **10** and **11**. (Toluene-d_8, 5V% (0.543 M), room temperatrure, **1-HG2** 1 mol%, **3** (4.34 M, 8 equiv.)).

Following the investigations of ROCM of **CPD** with *cis*-stilbene (**3**) our attention turned to synthesis of high value chemicals such as hexa-2,4-diene-1,6-diyl diacetate (**8**) – a 1,6-hexandiol precursor – and 1,3-butadiene (**BD**). Reactions have been carried out at 25 °C using commercially available **1** catalyst (0.05 and 1 mol%) systems in 5 V% **CPD** toluene solutions (0.543 M) by using of coupling agents *cis*-butene diol diacetate (**2**) and **ethylene** (Table 2 and 3).

Table 2. Conversion of **CPD** and yields of **8** and **9** at room temperature using commercially available Grubbs catalyst systems. (Toluene solution, 5 V% CPD (0.543 M), 3 h, the yields were determined by 1H NMR)

Entry	**1** Cat.	**1** (mol%)	**2** equiv.	**CPD** conv. (%)	**8** (%)	**9** (%)	TON (of **8**)
1[a]	**G3**	1	1	77	~6	~20	~6
2[a]	**G3**	1	2	88	~8	~21	~8
3	**G3**	1	4	97	24	31	24
4	**G3**	1	6	>98	48	58	48
5	**G3**	1	8	>98	67	68	67
6	**HG2**	1	8	>98	68	61	68
7	**G2**	1	8	84	59	52	59
8	**G2**	0.05	8	74	47	44	940
9	**G3**	0.05	8	90	59	57	1180
10	**HG2**	0.05	8	91	56	57	1120

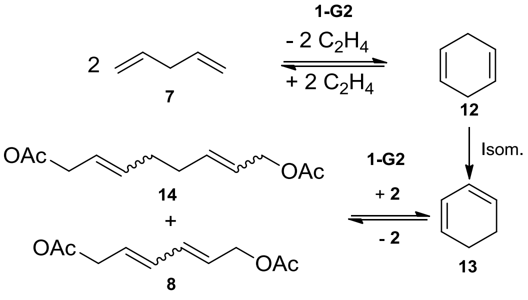
[a] Yields of **8** and **9** are estimated based on GC-MS (TIC).

Complete conversion of **CPD** and the formation of **8** and **9** were observed with reasonable yield (67% and 68%) within three hours of reaction time (Table 2, Entry 3) using 1 mol% of **1-G3** catalyst loading and eightfold excess of **2**. When the reaction was carried out using **1-HG2** catalyst under the same conditions, similar yields were obtained (68% and 61%). Catalyst **1-G2** gave somewhat lower conversion (84%) and **8** and **9** product yields (59% and 52%) than the ones above. The GC-MS investigations of the hydrogenated reaction mixture indicated the formation of minor amount of the hydrogenated homologs of **8** and **9** (Figure S7).

Reproduction of the experiments at 0.05 mol% catalyst loading high **CPD** conversions (up to 91%) and relatively high turnover numbers (TONs) were observed (940 – 1180) (Table 2). The hydrogenation of the reaction mixture has been carried out according to standard procedure giving 1,6-hexanediol diacetate and 1,7-heptanediol diacetate in quantitative yields.[57] When the reactions were carried out at 0.01 mol% catalyst loading, low **CPD** conversions and only traces amount of the reaction products were observed.

Carrying the reaction out in the presence of stoichiometric amount of **2**, beside **5** primary metathesis products, **8** and **9** were formed in reasonable yield (6% and 20%), meanwhile the CPD conversion was 77%. Some precipitation – supposedly oligomerization – was noticed. At extended reaction time (24 h), the formation of a substantial amount of **12** (40%) and a complete **CPD** conversion were detected. When the excess of **2** was gradually increased, higher yields of secondary metathesis products (**8** and **9**) (up to 68%, Table 2) were observed (at three hours reaction time), meanwhile only traces amount of **12** formed according to ^{1}H NMR.

The ethenolysis[58–60] of **CPD** (0.543 M) was carried out using 1 or 5 mol% of **1-G2** at room temperature and 10 bar of ethylene pressure. Considering the solubility of the ethylene in toluene under the applied reaction condition (10 bar and 25 ˚C), 2.6 mole equivalent (1.55 M) ethylene could be calculated to one mole **CPD**.[61,62] As the ethylene could be used in this slight excess, only a moderate **CPD** conversion and an equilibrium mixture of the primary and secondary metathesis products were expected. Indeed, beside some unreacted **CPD** the formation of **BD**, 1,4-pentadiene (**7**) and 1,3,6-heptatriene (**4**) were observed in reasonable yield (Table 3).



Scheme 4. Conversion of **7** to **8** and **14**.

Although, the conversion of **CPD** was moderate (50-73%), the ROCM metathesis product formation was almost exclusive. The extension of the reaction time from 3 to 12 hours resulted in slightly higher **CPD** conversion (from 46 to 58%), however longer than 12 hours of reaction time at 1 mol% catalyst loading had no additional effect on the **CPD** conversion. It should be noted that beside the expected reaction products **BD**, **4** and **7**, the formation of **12** was also considerable due to self-metathesis of **7** or **CPD** oligomers (Scheme 3). Although **12** has low activity in metathesis, it can be isomerized to 1,3-cyclohexadiene (**13**),[63] which readily goes to metathesis reaction with **2** giving an additional amount of **8** and tetradehydro-1,8-octanediol diacetate (**14**) (Scheme 4).

Ethenolysis of **CPD** at relatively high (5 mol%) catalyst loading and extended reaction time (120 h) gave higher **CPD** conversion and higher yield of the secondary metathesis products (**BD** and **7**) than above. Considering that **12** is a low-strained cycloolefin, one would expect that the corresponding equilibrium should be fully shifted to the formation of **12**. Thus, it could be presumed that the overall reaction mixture should end up with quantitative amount of **12**. However, the quantitative formation of **12** was never observed in repeated ethenolysis tests (Table 3) even at relatively high catalyst loadings and extended reaction time.

Table 3. Ethenolysis of **CPD**. (**1-G2** (1-5 mol%), room temperature, p = 10 bar of ethylene (1.55 M), in toluene as solvent, CPD 5 V%, 0.543 M) (L: liquid, G: gas phase). (CPD conversion is determined by 1H NMR. The yields of the reaction products were estimated based on GC integral areas using FID and/or MS detectors)

t (h)	**1-G2** (mol%)	**CPD** conv. (%)	**BD** (L) (%)	**BD** (G) (%)	**7** (L) (%)	**4** (L) (%)	**12** (L) (%)
3	1	46±6.0	11±1.5	2.6± 1.0	20.0 ±5.9	13.0±6.9	1.2±0.47
12	1	58	12.8	2.5	25.2	23.2	1.8
20	1	60	12.4	2.3	24.0	20.4	1.1
120	5	73	15.6	8.0	35.2	16.1	6.1

Theoretical calculations have been carried out to rationalize the experimentally observed conversions in the ROCM of **CPD** with **2**, **3** and **ethylene**. Standard reaction free energy (with reference state c_0 = 1M) and equilibrium constant for all reaction steps in Scheme 5 were calculated at DLPNO-CCSD(T)/cc-pVTZ theory level[64,65] (using M06-2X/cc-pVTZ geometry and frequencies with scaling)[63,64] and as a mean of the results of G3, G4 and CBS-APNO (for the ethylene path) theories[68–70] with hindered rotor corrections[71] and using an implicit toluene solvent model.[72,73] See details in the S.I. The free energy diagram of the synthesis paths are shown in Fig. 3 for the favored all-trans product isomers (e.g. **4**^{E}, **9**^{EE}, **5**^{EEE}).

In accordance with the expectations, theoretical calculations predict rather high, $K_3^{1/2}$=40M$^{1/2}$ value for the formation of **12** (1/2 mol) and **ethylene** from **7**. Obviously, thermodynamic equilibrium is not reached for this reaction, because k_3 is supposedly slow comparing to k_2 and k_1 and most probably the catalyst decomposes before the full conversion of **7**. Furthermore, it is well-known that the ruthenium methylidene (R=CH$_2$) intermediate is quite unstable, which may affect the overall catalyst performance.[74–76] The same reasons can lie behind the observed moderate conversions to **12** in the other two synthesis paths.

Considering the theoretical analysis of ROCM of **CPD** with **2** and **3** it can be concluded that the relatively high yield for the secondary metathesis products (**8**, **9** and **10**, **11**) – assuming that the chemical equilibrium is reached for the corresponding metathesis steps after long enough reaction time – are aligned with calculated relative high K_2 = 2 and 220 equilibrium constants (Figure 3). Nevertheless, when **ethylene** is used as cross-coupling agent K_2 is slightly lower than 1 (K_2 = 0.37), which is consistent with the observed significantly higher amount of primary metathesis product considering a high, ~1.55 M solubility of ethylene at 10 bar. (See details on solvation and chemical equilibrium calculations in the S.I.) The equilibrium constant for the formation of 1,3,5 hexatriene, **15** (1/2 mol) is $K_4^{1/2}$=1.5, thus also close to 1, which is qualitatively in line with its observed formation. As it can be seen in Table 3, the overall yield of **BD** is always lower than that of **7** and **12**. This can be explained by the self-metathesis of **BD** giving polyunsaturated compounds including **15**, which could be clearly observed in the GC-MS TIC of the reaction mixture.[77,78]

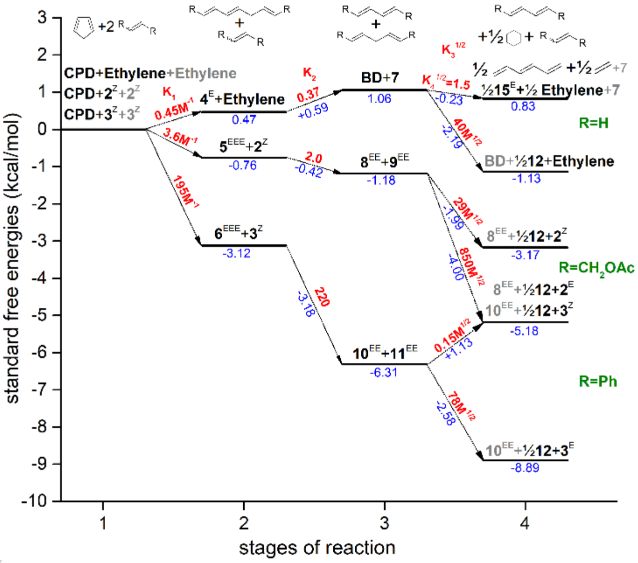


Figure 3. Theoretically determined free energy diagram of the three synthesis paths. Species indices, standard free energy changes and equilibrium constant of reactions are shown in black, blue and red, resp. Species indices not participating in a reaction step are printed in grey.

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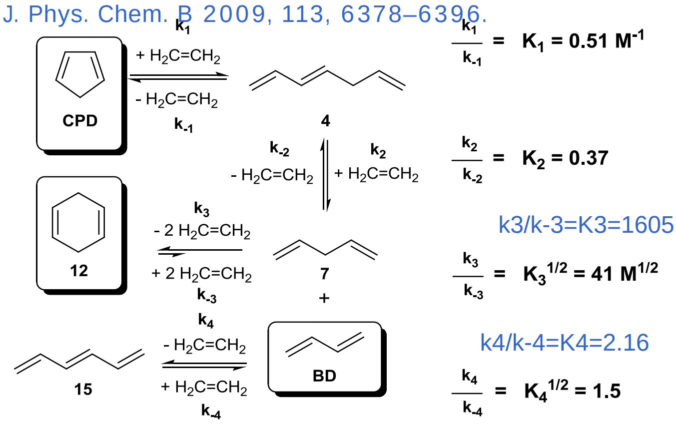

k3/k-3=K3=1605M

k4/k-4=K4=2.16

Scheme 5. Formation of **12** via the ethenolysis of **CPD** and the calculated K values.

Conclusions

A novel tandem reaction of **CPD** leading to value added linear polyolefins has been demonstrated. It has been shown that **CPD** can be readily converted to high value chemicals such as 1,6-hexandiol polyurethane monomer and 1,3-butadiene (**BD**) in reasonable yields via ruthenium-catalyzed tandem ROCM and CM reactions at low catalyst loading and ambient reaction conditions (TON up to 1180). The reaction product composition strongly depends on the applied reaction time and the excess of the cross-coupling agents. When the tandem ROCM/CM of **CPD** is carried out in the presence of stochiometric amount or slight excess of cross coupling agents (**Ethylene**, **2** or **3**) at extended reaction time **CPD** oligomerization (giving a non-soluble solid), some secondary metathesis products and 1,4-cyclohexadiene (**12**) formation occur. When relatively short reaction time (3h) and high excess of cross-coupling agents applied the target, secondary metathesis products (e.g. **8** and **9**) form in reasonable yield (up to 68%). The primary metathesis products (**4**, **5**, or **6**) could always be detected, however the secondary metathesis products are always the major components of the reaction mixture. Theoretical calculations indicated that the relatively high yields for the secondary metathesis products (**8**, **9** and **10**, **11**) are most apparently due to the relative high K_2 = 2 and 220 equilibrium constants (Figure 3 and Scheme 5).

Experimental Section

General information. All reactions were conducted under nitrogen atmosphere using Schlenk-technique or under argon atmosphere in an MBraun (Labmaster PRO) glovebox. **1-G2**, **1-HG2** (Materia), palladium on carbon, dicyclopentadiene, *cis*-stilbene (**3**), ethylbenzene (**EB**) and other solvents (Aldrich), $CDCl_3$, toluene-d_8 (Eurisotop) were used as received. **1-G3** was synthetized according to literature procedure.[79] **CPD** was freshly cracked from **DCPD** at 210°C. Gaseous components were collected from the Fischer-Porter Bottle to a Multi-Layer Foil Gas Sampling Bag (Restek). The overall yield and conversion were determined for each reaction product using ^1H NMR with **EB** as internal standard. Routine ^1H NMR spectra were obtained on a Varian Unity INOVA spectrometer operating at an equivalent ^1H frequency of 500 MHz. GC-MS analyses were carried out using a Shimadzu GC-MS-QP2010 instrument fitted with a Rxi-5Sil MS column coupled with a quadrupole mass filter with pre-rods. The gaseous reaction products were analyzed on-line by a Shimadzu GC-2010 gas chromatograph (GC) equipped with a 50-m HP-PLOT-Fused Silica column (Al_2O_3, KCl), flame ionization detector (FID). The GC column was calibrated for 1,3-butadiene (**BD**).

***In-situ* ^{1}H NMR investigation of the Diels Alder reaction of CPD with 3 in toluene**. A Schlenk tube was charged with toluene- d_8 (0.2 mL), **EB** (45 mL, 0.34 mmol), *cis*-stilbene (**3**) (0.77 mL, 4.32 mmol, 8 equiv. of **CPD**) and **CPD** (45 mL, 0.54 mmol). The colorless solution was transferred into a screw-capped NMR tube under nitrogen and ^1H NMR spectra were recorded over six hours (t[min]= 15, 30, 45, 90, 180, 240, 300) at room temperature. Based on the ^1H NMR spectra of the mixture, no reactions were observed in six hours such as dimerization of **CPD**.

Representative example of the ROCM of CPD with *cis*-stilbene (3): A Schlenk tube was charged with **1-G3** (4.8 mg, 1 mol%), toluene-d_8 (0.2 mL), **EB** (45 mL, 0.34 mmol), **3** (0.77 mL, 4.32 mmol) and **CPD** (45 mL, 0.54 mmol). The brown solution was transferred into a screw-capped NMR tube under nitrogen and ^1H NMR spectra were collected over six hours (t[min]= 14, 26, 40, 49,69, 102, 129, 192, 257, 308) at room temperature. ^1H NMR of the products **10** and **11** were in agreement with literature data (Figure 1).[80-83] After 24 hours, part of the reaction mixture (0.1 mL) was hydrogenated over Pd/C in EtOH and the reaction mixture was analyzed by GC-MS measurements.

Representative example of the ROCM of CPD with *cis*-butene diol diacetate (2). A screw-cap NMR tube under argon was charged with **2** (0.72 mL, 4.5 mmol), toluene-d_8 (0.15 mL), **EB** (50 mL, 0.38 mmol) and **CPD** (50 mL, 0.59 mmol). After the initial ^1H NMR measurement of the starting materials, the solution of the appropriate catalyst (5 mg **1-G2**, 0.0059 mmol, 1 mol%) in toluene-d_8 (0.1 mL) was added into the mixture. After 3h *in situ* ^1H NMR spectrum was taken (Table 2). An aliquot of the reaction mixture (0.1 mL) was hydrogenated over Pd/C in EtOH and the reaction mixture was analyzed by GC-MS measurements.

Representative example of the ethenolysis of CPD. A Schlenk tube was charged with toluene (1.6 mL), **EB** (200 mL, 1.52 mmol) under argon. **CPD** (200 mL, 2.3 mmol) was added under nitrogen. The mixture was transferred to a Fischer-Porter bottle and the solution (toluene, 2.0 mL) of the catalyst (20 mg **1-G2**, 0.024 mmol) was added. The bottle was flushed four times with ethylene before the final ethylene pressure was applied. After a period of time, the gaseous products were collected in an airtight gas sampler bag and analyzed by GC (FID). The mixture was quenched with ethyl vinyl ether and the liquid phase was analyzed by GC-MS. Another part of the liquid phase was diluted with $CDCl_3$ and analyzed by ^1H NMR (Table 3).

ROCM of 1,3-cyclohexadiene (13) with 2. A screw-capped NMR tube was charged with **2** (1.1 mL, 6.7 mmol), toluene-d_8 (0.3 mL), **EB** (50 mL, 0.38 mmol) and **13** (53 mL, 0.56 mmol) under argon. After the initial ^1H NMR measurement of the starting materials, the solution of the catalyst (3.5 mg **1-HG2**, 0.0057 mmol) in toluene-d_8 (0.1 mL) was added to the mixture. After 5 hours of reaction time, ^1H NMR spectrum was taken of the reaction mixture indicating 71% conversion of **13** and the formation of **8** (36%) and **14** (56%) (Figure S14). An aliquot of the sample (0.1 mL) was hydrogenated over Pd/C in EtOH and analyzed by GC-MS.

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Keywords: Tandem reaction • ROCM • CM • ruthenium • metathesis • cyclopentadiene • butadiene • 1,6-hexandiol

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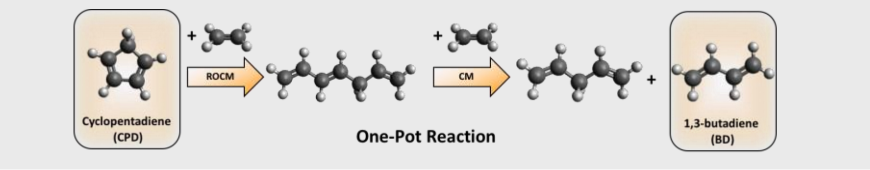

A novel cyclopentadiene (**CPD**) tandem Ring Opening Cross Metathesis (ROCM) and Cross Metathesis (CM) reaction leading to linear polyolefins is presented. This reaction opens new applications area of **CPD** leading to high value chemicals.

*Gábor Turczel, Ervin Kovács, Eszter Csizmadia, Tibor Nagy, Imre Tóth, Robert Tuba**

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One-pot Synthesis of 1,3-Butadiene and 1,6-Hexandiol Derivatives from Cyclopentadiene (CPD) via Tandem Olefin Metathesis Reactions