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# In Tandem or Alone: a Remarkably Selective Transfer Hydrogenation of Alkenes Catalyzed by Ruthenium Olefin Metathesis Catalysts

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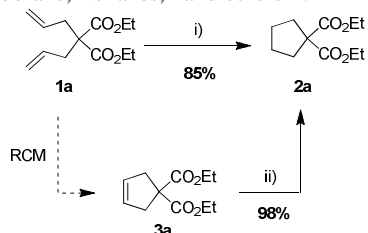
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Dedicated to Professor Mieczysław Mąkosza on the occasion of his 80<sup>th</sup> birthday.

**A system for transfer hydrogenation of alkenes, composed from a ruthenium metathesis catalyst and HCOOH is presented. This operationally simple system can be formed directly after a metathesis reaction to effect hydrogenation of the metathesis product in a single pot. These hydrogenation conditions are applicable to a wide range of alkenes and offer remarkable selectivity.**

Catalytic hydrogenation of olefins is one of the most important "classics" in organic chemistry.<sup>1</sup> Due to high complexity of targets approached by contemporary organic synthesis, there is a very high demand for chemo- and regioselective methods to hydrogenate C–C multiple bonds in the presence of many other functionalities, including other olefinic moieties. A difficulty associated with catalytic hydrogenation is the use of hydrogen gas, whose physical properties complicate its safe, efficient and economical storage. This creates a need for new selective, safe and environmentally friendly hydrogenation methodologies. Recently reduction of olefins has been carried out in a homogeneous fashion using transition metals (incl. Rh,<sup>2a</sup> Ir,<sup>2b</sup> Ru,<sup>2c-f</sup> Pd<sup>2g</sup>) and gaseous H<sub>2</sub> or hydrogen sources such as alcohols,<sup>2h</sup> hydrazine,<sup>2i</sup> formic acid–triethylamine azeotrope,<sup>2j</sup> ammonia–borane,<sup>2k</sup> silanes,<sup>2l</sup> and others<sup>2m</sup>.

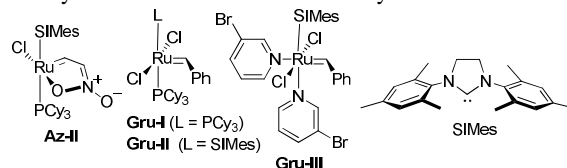


**Scheme 1.** Observed Reactivity of Azinate Complex **Az-II**.<sup>8</sup> Conditions: i) 1. **Az-II** (1 mol%), C<sub>2</sub>Cl<sub>6</sub> (4 mol%), THF, 80 °C, 3 h; 2. **Az-II** (1 mol%), NaH (0.1 equiv.), HCOOH (50 equiv.), THF, 80 °C, 20 h; ii) **Az-II** (2 mol%), NaH (0.1 equiv.), HCOOH (50 equiv.), 80 °C, 20 h.

Over the past two decades olefin metathesis has transformed the design and practice of organic synthesis.<sup>3</sup> It should be noted that this reaction can be easily incorporated in tandem processes, where the metathesis catalyst is triggered for a second transformation.<sup>4</sup> One of such sequences is metathesis–hydrogenation, typically conducted under high pressure of hydrogen, which is required to convert Ru

alkylidene complexes into a hydrogenation catalyst.<sup>5</sup> Recently a more convenient protocol, using NaBH<sub>4</sub> as hydrogen source has been reported.<sup>6</sup>

During our study on a new chelating ruthenium azinate complex (**Az-II**, Figure 1), we have noticed its reactivity in numerous transformations.<sup>7</sup> Depending on the conditions applied, the same complex promoted efficiently olefin metathesis, isomerization, cycloisomerization or reduction of a carbonyl group.<sup>7</sup> Serendipitously, we have found recently that after the metathesis step is promoted by **Az-II**, adding sodium hydride and formic acid to the reaction mixture leads to a new catalytic system that is capable of efficient reduction of cycloolefins (Scheme 1).<sup>8</sup> Intrigued by this preliminary observation we decided to study it in a more detail.



**Fig. 1.** Selected Ruthenium Olefin Metathesis Catalysts (Cy = cyclohexyl).

Since the azinate complex **Az-II** is not commercially available, in the present study we decided to check if other, more standard Ru-alkylidene complexes, can also show a similar reactivity in the presence of HCOOH<sup>9a</sup>, so can be used in transfer hydrogenation or in olefin metathesis–hydrogenation sequences. To do so, three generations of representative Grubbs' catalysts **Gru-I**, **Gru-II** and **Gru-III** have been selected (Fig. 1) and tested in a model reduction of cyclopentene **3a** to cyclopentane **2a** (Table 1). After some initial experiments, an optimized procedure was elaborated, as follows: to a solution olefin **3a** catalyst (2 mol%), base (0.2 equiv.) was introduced, followed immediately by 98% formic acid (50 equiv. relative to olefin). After The reaction mixture was heated to 80 °C for 6 h in a sealed flask.<sup>9b</sup> After screening Ru-catalysts presented in Figure 1, complex **Gru-II**, promoting hydrogenation at comparable rate as the azinate complex **Az-II**, was chosen for the further studies. The role of base (Table 1, entries 5 – 8) and solvent (entries 9 – 11) was also investigated to find that sodium hydride can be replaced by sodium formate and the reaction can be conducted in solvents like THF, dimethyl carbonate, dimethoxyethane or dichloroethane.

To check, if this reduction can be applied one-pot together with olefin metathesis event, we conducted the RCM reaction of diene **1a** in the presence of 2 mol% of **Gru-II** in THF at 40 °C. After 30 minutes, TLC revealed that the olefin metathesis step was complete. At this point 0.2 equiv. of HCOONa was added to the reaction mixture, followed by immediate addition of 50 equiv. of HCOOH. The reaction tube was closed and heated to 80 °C. After 7 hours the reduction was completed, as shown by NMR. Using this procedure, RCM–transfer hydrogenation experiments were conducted with a small set of dienes, producing, after aqueous work-up, corresponding cycloalkanes in good to excellent yield (Table 2).

**Table 1.** Optimization of a Model Hydrogenation Reaction of **3a** to **2a**.<sup>a</sup>

Entry	Catalyst	Base	Solvent <sup>b</sup>	NMR Yield [%] <sup>c</sup>
1	<b>Az-II</b>	NaH	THF	92
2	<b>Gru-I</b>	NaH	THF	27
3	<b>Gru-II</b>	NaH	THF	>99
4	<b>Gru-III</b>	NaH	THF	95
5	<b>Gru-II</b>	none	THF	68
6	<b>Gru-II</b>	<i>t</i> -BuOK	THF	90
7	<b>Gru-II</b>	HCOONa	THF	>99
8	<b>Gru-II</b>	NaOH	THF	78
9	<b>Gru-II</b>	NaH	DMC	>99
10	<b>Gru-II</b>	NaH	DME	92
11	<b>Gru-II</b>	NaH	DCE	>99

<sup>a</sup> Conditions: Catalyst (2 mol%), base (0.2 equiv.), HCO<sub>2</sub>H (50 equiv.), solvent, 80 °C, 6 h. <sup>b</sup> DMC = dimethyl carbonate; DME = 1,2-dimethoxyethane; DCE = 1,2-dichloroethane. <sup>c</sup> Yield determined by <sup>1</sup>H NMR.

**Table 2.** Sequence of RCM–Transfer Hydrogenation Catalysed by **Gru-II**.<sup>a</sup>

Entry	Substrate	Product	Time [h] <sup>b</sup>	Yield [%] <sup>c</sup>
1			7.5	99 <sup>d</sup>
2			20.5	97 <sup>e</sup>
3			7.5	92 <sup>e</sup>
4 <sup>f</sup>			6.5	89 <sup>d</sup>

<sup>a</sup> Conditions: i) **Gru-II** (2mol%), THF, 40 °C, 30 min, then ii) HCOONa (0.2 equiv.), HCOOH (50 equiv.), 80°C, THF. <sup>b</sup> Time of RCM (0.5 h) + time of reduction. <sup>c</sup> Yield of spectrally pure isolated products. In all cases full conversion was observed. <sup>d</sup> Product isolated by extraction. Crude product was spectrally pure. <sup>e</sup> Product purified by silica gel column chromatography. <sup>f</sup> NaH was used instead of HCOONa.

To examine deeper the substrate scope of this transfer hydrogenation reaction, a number of unsaturated substrates was subjected to the optimised reaction conditions. A range of substrates can be hydrogenated efficiently with this system (Table 3), proving excellent compatibility with a number of functional groups.

**Table 3.** Hydrogenation of Cyclic and Acyclic Unsaturated Substrates.<sup>a</sup>

Entry	Substrate	Product	Time [h]	Yield. [%] <sup>b</sup>
1			6	99 <sup>c,d</sup>
2			6	99 <sup>d</sup>
3			6	98 <sup>e</sup>
4			20	98 <sup>c,f</sup>
5			24	90 <sup>f</sup>
6 <sup>g</sup>			48	74 <sup>e</sup> (100)
7			6	83 <sup>e</sup>
8			6	91 <sup>h</sup>
9 <sup>i</sup>			336	43 <sup>f</sup> (100)
10 <sup>i</sup>			120 336	(50) (80)
11 <sup>i</sup>			48	96 <sup>e</sup>
12			6	99 <sup>d</sup>

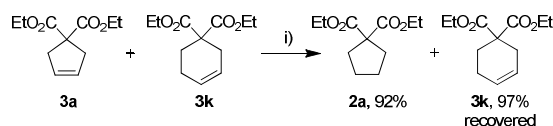
<sup>a</sup> Conditions: **Gru-II** (2 mol%), HCOONa (0.2 equiv.), HCOOH (50 equiv.), 80°C, THF. <sup>b</sup> Yields of spectrally pure isolated products. In parenthesis are conversions determined by <sup>1</sup>H NMR, where not indicated full conversion was observed. <sup>c</sup> NaH was used instead of HCOONa. <sup>d</sup> Product isolated by extraction. Crude product was spectrally pure. <sup>e</sup> Product purified by silica gel column chromatography. <sup>f</sup> Product purified by bulb-to-bulb distillation. <sup>g</sup> Reaction with 3 mol% of **Gru-II**. <sup>h</sup> Product purified by crystallization. <sup>i</sup> Reaction with 4 mol% of **Gru-II**.

Interestingly, carbonyl functions in ketones<sup>10</sup> and enones (Table 3, entries 3 – 4 and 7 – 8) do not undergo reduction under these conditions, which makes our system different from the previously described [Ru]/NaBH<sub>4</sub> couple.<sup>6</sup> As suggested by experiment conducted with **3f**, primary and secondary benzyl ethers and an allylic stereocenter survived the reaction untouched (Table 3, entry 5). Interestingly, compounds bearing unprotected OH group **3g** (Table 3, entry 6) underwent transfer hydrogenation quantitatively and no esterification process took place. Reaction of enones **3h**, **3i**

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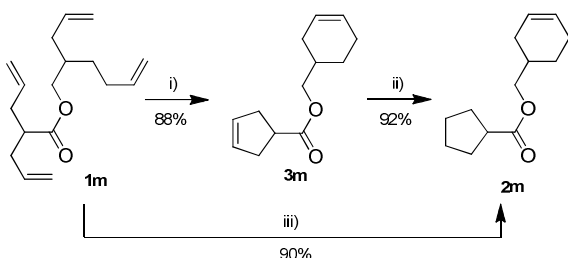
and  $\alpha,\beta$ -unsaturated ester **3l** under our conditions lead to reduction of conjugated C-C double bond (Table 3, entries 7 – 8, 11). Despite of being more reluctant to transfer hydrogenation, ester **3l** lead to high isolated yield of corresponding product **2l**. The second, more substituted C-C double bond present in  $\beta$ -damascone (**3h**) stayed untouched. Hydrogenation of trisubstituted double bond in **3j** proceeds much slower, requiring 336 h for completion (43% isolated yield, entry 9).<sup>11</sup> The surprise came, however, when we attempted the reduction of cyclohexene derivative **3k**. Hydrogenation rates of small ring cycloalkenes depends on their strain energies,<sup>12a</sup> and in the case of reduction by diimide, it was shown that the relative rate of cyclopentene hydrogenation is 15.5 times faster than the rate of cyclohexene reduction.<sup>12b</sup> However, in the case of **3k** the reaction was *not complete* even after 336 h (14 days) of heating at 80 °C, while both cyclopentene (entry 11) and cycloheptene rings (entry 12) were fully reduced in 6 hours. Of note, cyclohexene ring is easily reduced by the newly published system composed of NaBH<sub>4</sub> and Ru olefin metathesis catalyst.<sup>6</sup>

We speculated that the observed high sensitivity of **Gru-II**/HCOOH catalytic system towards ring strain and substitution pattern can be utilised for selective reduction of one C-C double bond in the presence of the others. To explore this interesting possibility, a cross-over experiment, shown in Scheme 2, was executed. Despite the reaction presented in Scheme 2 has no synthetic interest, it demonstrates the level of control offered by this transfer hydrogenation system. An equimolar mixture of **3a** and **3k** was subjected to transfer hydrogenation process leading to complete reduction of the cyclopentene ring, with practically no reduction of a cyclohexene double bond under this conditions (Scheme 2).



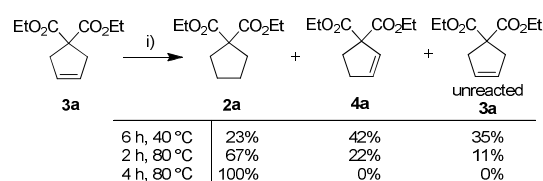
**Scheme 2.** Competition study. Conditions: i) **Gru-II** (2 mol%), HCOONa (0.2equiv.), HCOOH (50 equiv.), THF, 4 h, 80°C. Conversion determined by GC using internal standard.

While the system studied by us shows high level of selectivity, it offers also an additional possibility of being readily coupled with olefin metathesis reactions. An example shown in Scheme 3 starts with Ru-catalysed double-RCM of tetraene **1m** forming selectively product **3m** bearing one five- and one six-membered unsaturated ring. Then, *only one of two seemingly very similar C-C double bonds* present in **3m**, was selectively reduced by **Gru-II**/HCOOH, yielding mono-saturated product **2m** in good yield (Scheme 3, route i+ii). The same two-step sequence can be easily conducted in one pot fashion, converting directly tetraene **1m** into semihydrogenated cyclohexene derivative **2m** in 90% yield (Scheme 3, route iii).



**Scheme 3.** Tandem Double RCM-Selective Transfer Hydrogenation of **1m**. Conditions: i) **Gru-II** (2 mol%), DCM, 1 h, 40 °C. ii) **Gru-II** (2 mol%), HCOONa (0.2 equiv.), HCOOH (50 equiv.), THF, 4 h, 80 °C. iii) **Gru-II** (2 mol%), THF, 0.5h, 40 °C, then HCOONa (0.2 equiv.), HCOOH (50 equiv.), THF, 4 h, 80 °C.

The precise details of the nature of catalytic species produced upon action of HCOONa/HCOOH are unclear. It was reported that some Ru complexes can catalyse decomposition of formic acid leading to formation of CO<sub>2</sub> and ruthenium hydride species.<sup>13</sup> This suggests, that entry into the catalytic cycle starts with conversion of **Az-II** or **Gru-II** into Ru-hydride species, that act as actual hydrogenation catalyst.<sup>14,15</sup> Similar mechanism was also suggested for other Ru-catalysed transfer hydrogenation reactions.<sup>6</sup> To prove the existence of Ru-H species in our system Grubbs second generation catalyst was placed in a dry NMR tube containing formic acid (20 equiv) in THF-d<sub>8</sub>. Then the tube was closed and the reaction mixture was heated at 50 °C for 4h. After that time the tube was cooled down to room temperature and NMR spectrum was measured. A new signal with chemical shift of -6.86 ppm has appeared. This chemical shift is in the range characteristic for ruthenium hydride species.<sup>16</sup> In line with this observation, in hydrogenations of **3a** analysed before the end of reaction was reached, we observed some amounts of product **4a** formed *via* alkene isomerisation process (C-C double bond migration)<sup>17</sup> that were decreasing with time (Scheme 4). Both these observations suggest presence of Ru hydride species during reduction with the Ru/HCOOH system described by us.



**Scheme 4.** Incomplete Isomerisation-Hydrogenation of **3a**: Conditions: i) **Gru-II** (2 mol%), NaH (0.2 equiv.), HCOOH (50 equiv.), THF. Conversion determined by <sup>1</sup>H NMR.

## Conclusions

In conclusion, a mild protocol for transfer hydrogenation of alkenes has been demonstrated, that exhibits high functional group tolerance and surprising selectivity. For a number of alkenes, Ru/HCOOH system can be seen as a safe alternative to dangerous pressurized hydrogen gas. This method can be also coupled with olefin metathesis events, allowing for efficient one-pot sequences. Unlike other Ru-catalysed hydrogenations protocols, Ru/HCOOH allows for selective reduction of a given C-C double bond in the presence of a relatively similar ones and is compatible with keto and enone functionalities, that can be reduced by NaBH<sub>4</sub>. Therefore the highly selective nature of this system provides an useful addition to the still expanding<sup>6</sup> repository of hydrogenation methods.

## Experimental section

**Procedure A. Reduction of C-C Double Bonds.** Olefin (1 mmol) and 5mL of anhydrous THF were placed under argon in a reaction tube. Next, catalyst **Gru-II** (2 mol%) was added to resulting solution followed with addition of HCOONa (0.2 mmol) and 98% HCOOH (50 mmol) and the reaction tube was closed. The reaction mixture was stirred for appropriate period of time at 80 °C, then allowed to reach room temperature and poured into saturated aqueous solution of NaHCO<sub>3</sub> (ca. 30 mL). The aqueous layer was extracted with an appropriate organic solvent organic solvent and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated *in vacuo* to obtain the crude product, which was purified when necessary by column chromatography or by bulb-to-bulb distillation.

**Diethyl cyclopentane-1,1-dicarboxylate (2a).** Spectrally pure product was synthesized according to procedure B without further purification (212 mg, 99%) using **3a** as a starting material and NaH instead of HCO<sub>2</sub>Na. Analyses of product were in accordance with previously reported.<sup>18</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 4.20-4.12 (m, 4H), 2.21-2.11 (m, 4H), 1.71-1.62 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 172.7, 61.1, 60.4, 34.4, 25.4, 14.0.

**1-(2,6,6-Trimethylcyclohex-1-en-1-yl)butan-1-one (2h).** Spectrally pure product was synthesized according to procedure A using commercially available substrate **1h** without further purification (161 mg, 83%). Analyses were in accordance with previously reported.<sup>19</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 2.50 (t, *J* = 7.4 Hz, 2H), 1.93 (t, *J* = 6.3 Hz, 2H), 1.69-1.59 (m, 4H), 1.53 (s, 3H), 1.45-1.39 (m, 2H), 1.04 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 212.0, 143.6, 128.7, 47.8, 39.0, 33.3, 31.2, 28.8, 20.95, 19.0, 16.7, 13.9.

**Procedure B. Tandem Olefin Metathesis and C-C Double Bond Reduction.** Diene (1 mmol) and in 5 mL of dry THF were placed in a reaction tube. Catalyst **Gru-II** (2 mol%) was added and the ring closing metathesis reaction was carried out for 0.5 h at 40 °C. Once the RCM reaction was completed according to TLC or GC, solid HCOONa (0.2 mmol) was added immediately followed by 98% HCOOH (50 mmol) and the reaction was continued for appropriate period of time at 80 °C in a closed tube, then allowed to reach room temperature and poured into saturated aqueous solution of NaHCO<sub>3</sub> (ca. 30 mL). The aqueous layer was extracted with an appropriate organic solvent and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated *in vacuo* to obtain the crude product., which was further purified when necessary by column chromatography or by bulb-to-bulb distillation.

**Diethyl cyclopentane-1,1-dicarboxylate (2a).** Product was synthesized according to procedure B using diene **1a** as a starting material and NaH instead of HCO<sub>2</sub>Na. Spectrally pure product was isolated by extraction (214 mg, 99%). Analyses were in accordance with previously reported.<sup>18</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 4.20-4.12 (m, 4H), 2.21-2.11 (m, 4H), 1.71-1.62 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 172.7, 61.1, 60.4, 34.4, 25.4, 14.0.

**Benzoylcyclopentane (2c).** Product was synthesized according to general procedure B using diene **1c** as a starting material. Purification by using column chromatography afforded spectrally pure product **2c** (160 mg, 92%). Analyses were in accordance with previously reported.<sup>20</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.03-7.93 (m, 2H), 7.60-7.50 (m, 1H), 7.50-7.42 (m, 2H), 3.72 (quint, *J* = 7.88 Hz, 1H), 2.06-1.85 (m, 4H), 1.83-1.54 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 202.9, 137.0, 132.8, 128.6, 128.6, 46.5, 30.1, 26.4.

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- 9 a) Formic acid is considered as viable and renewable feedstock for hydrogen. Ru(II) promoted catalytic formic acid dehydrogenation to gaseous mixture of H<sub>2</sub> and CO<sub>2</sub> was reported: I. Mellone, M. Peruzzini, L. Rosi, D. Mellmann, H. Junge, M. Beller and L. Gonsalvi, *Dalton Trans.*, 2013, **42**, 2495; b) In an open flask, the same catalytic system (2 mol% **Gru-II**, 50 equiv. HCOOH and 0.2 equiv. of NaH) leads to formation of **2a** in 90% yield, however, after prolonged time of 15 hours. For detailed experimental procedures see Electronic Supporting Information (ESI)

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- 11 Interestingly, trisubstituted alkenes were reported to be inert to Ru-catalysed transfer hydrogenation, cf. Ref. 6

- 12 a) P. v. R. Schleyer, J. E. Williams and K. R. Blanchard, *J. Am. Chem. Soc.*, 1970, **92**, 2377; b) The relative ratio of reduction with diimide is 15.5 for cyclopentene, 1.0 for cyclohexene, 12.1 for cycloheptene and 17.0 for cyclooctene, while for 1-methylcyclohexene is only 0.11. See: c) E. W. Garbish, Jr, S. M. Schildcrout, D. B. Patterson and C. M. Sprecher, *J. Am. Chem. Soc.*, 1965, **87**, 2932.

- 13 a) N. Manashe, E. Salant and Y. Shvo, *J. Organomet. Chem.*, 1996, **514**, 97.; b) T. Koike and T. Ikariya, *Adv. Synth. Catal.*, 2004, **346**, 37.

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15. It cannot be excluded that both, the initial ruthenium metathesis catalyst, and its decomposition products after olefin metathesis step, are able to catalyse the hydrogen transfer reaction.

16. a) T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day and R. H. Grubbs, *J. Am. Soc. Chem.*, 2003, **125**, 2546; b) M. B. Dinger and J. C. Mol, *Eur. J. Inorg. Chem.*, 2003, 2827; d) D. Pinggen, M. Lutz and D. Vogt, *Organometallics*, 2014, **33**, 1623.

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17. For decomposition pathways of ruthenium olefin metathesis catalysts and related processes, see: a) S. H. Hong, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2004, **126**, 7414; b) S. H. Hong, D. P. Sanders, C. W. Lee and R. H. Grubbs, *J. Am. Chem. Soc.*, 2005, **127**, 17160; c) S. H. Hong, A. G. Wenzel, T. T. Salguero, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2007, **129**, 7961.
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