PAPER

In tandem or alone: a remarkably selective transfer hydrogenation of alkenes catalyzed by ruthenium olefin metathesis catalysts†‡

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A system for transfer hydrogenation of alkenes, composed of 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 olefins are one of the most important "classics" in organic chemistry.[1] 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,[2a] Ir,[2b] Ru,[2c–f] Pd[2g]) and gaseous H_2 or hydrogen sources such as alcohols,[2h–j] hydrazine,[2k] formic acid–triethylamine azeotrope,[2l] ammonia–borane,[2m] silanes,[2n] and others.[2o,p]

Over the past two decades olefin metathesis has transformed the design and practice of organic synthesis.[3] It should be noted that this reaction can be easily incorporated in tandem processes, where the metathesis catalyst is triggered for a second transformation.[4] One such sequence is metathesis–hydrogenation, typically conducted under high pressure of hydrogen, which is required to convert Ru alkylidene complexes into a hydrogenation catalyst.[5] Recently a more convenient protocol, using $NaBH_4$ as a hydrogen source has been reported.[6]

During our study on a new chelating ruthenium azinate complex (**Az-II**, Fig. 1), we have noticed its reactivity in numerous transformations.[7] Depending on the conditions applied,
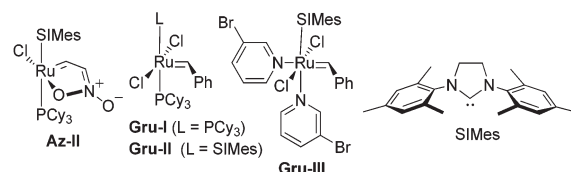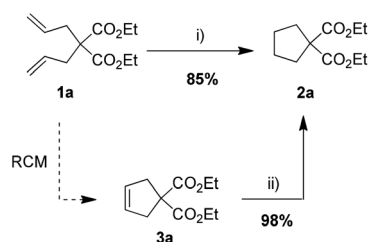

Fig. 1 Selected ruthenium olefin metathesis catalysts (Cy = cyclohexyl).

the same complex promoted efficiently olefin metathesis, isomerization, cycloisomerization or reduction of a carbonyl group.[7] 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).[8] Intrigued by this preliminary observation we decided to study it in more detail.

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,[9a] so can be used in trans-

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‡Electronic supplementary information (ESI) available: Full experimental details and characterization data, including NMR spectra. See DOI: 10.1039/c4ob02480j

Scheme 1 Observed reactivity of azinate complex **Az-II**.[8] Conditions: (i) 1. **Az-II** (1 mol%), C_2Cl_6 (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.

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Table 1 Optimization of a model hydrogenation reaction of **3a** to **2a**[a]

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

[a] Conditions: catalyst (2 mol%), base (0.2 equiv.), HCO$_2$H (50 equiv.), solvent, 80 °C, 6 h. [b] DMC = dimethyl carbonate; DME = 1,2-dimethoxyethane; DCE = 1,2-dichloroethane. [c] Yield determined by ^{1}H NMR.
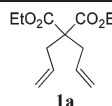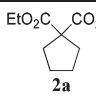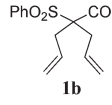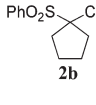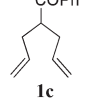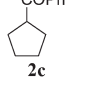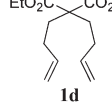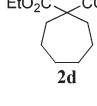
fer hydrogenation or in olefin metathesis–hydrogenation sequences. To do so, three generations of representative Grubbs' catalysts **Gru-I**, **Gru-II** and **Gru-III** have been selected (Fig. 1) and tested in a model reduction of cyclopentene **3a** to cyclopentane **2a** (Table 1). After some initial experiments, an optimized procedure was elaborated as follows: to a solution of olefin **3a** a catalyst (2 mol%), and a base (0.2 equiv.) were introduced, followed immediately by 98% formic acid (50 equiv. relative to olefin). Then the reaction mixture was heated to 80 °C for 6 h in a sealed flask.[9b] After screening Ru-catalysts presented in Fig. 1, complex **Gru-II**, promoting hydrogenation at a comparable rate as the azinate complex **Az-II**, was chosen for further studies. The roles of the base (Table 1, entries 5–8) and the solvent (entries 9–11) were 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 an 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).

To examine deeper the substrate scope of this transfer hydrogenation reaction, a number of unsaturated substrates were 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.

Interestingly, carbonyl functions in ketones[10] and enones (Table 3, entries 3, 4, 7 and 8) do not undergo reduction under these conditions, which makes our system different from the

Table 2 Sequence of RCM-transfer hydrogenation catalysed by **Gru-II**[a]

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

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

previously described [Ru]/NaBH$_4$ couple.[6] As suggested by the 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 took place. The reaction of enones **3h**, **3i** and α,β-unsaturated ester **3l** under our conditions lead to the reduction of conjugated C–C double bonds (Table 3, entries 7, 8 and 11). The second, more substituted C–C double bond present in β-damascone (**3h**) stayed untouched. Hydrogenation of the tri-substituted double bond in **3j** proceeds much slower, requiring 336 h for completion (43% isolated yield, entry 9).[11] However, we were surprised when we attempted the reduction of cyclohexene derivative **3k**. Hydrogenation rates of small ring cycloalkenes depend on their strain energies,[12a] 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.[12b] 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. It is noteworthy that the cyclohexene ring is easily reduced by the newly published system composed of NaBH$_4$ and Ru olefin metathesis catalysts.[6]

We speculated that the observed high sensitivity of the **Gru-II**/HCOOH catalytic system towards the ring strain and the substitution pattern can be utilised for selective reduction of one C–C double bond in the presence of others. To explore this interesting possibility, a competition experiment, shown in Scheme 2, was performed, to demonstrate the level of

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Table 3 Hydrogenation of cyclic and acyclic unsaturated substrates[a]

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

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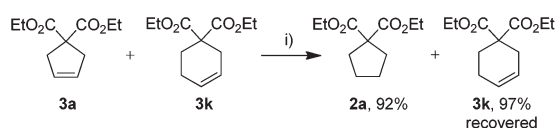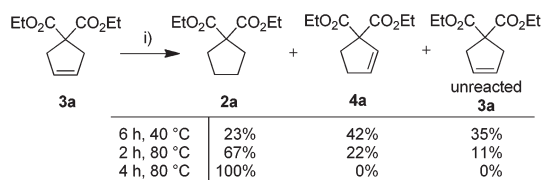
Scheme 2 Competition study. Conditions: (i) **Gru-II** (2 mol%), HCOONa (0.2 equiv.), HCOOH (50 equiv.), THF, 4 h, 80 °C. Conversion determined by GC using an internal standard.

3a + **3k** → **2a**, 92% + **3k**, 97% recovered
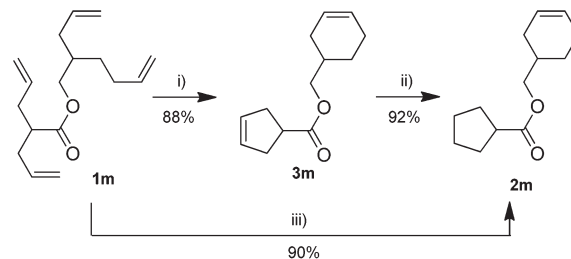
Scheme 3 Tandem double RCM-selective transfer hydrogenation of **1m**. Conditions: (i) **Gru-II** (2 mol%), DCM, 1 h, 40 °C. (ii) **Gru-II** (2 mol%), HCOONa (0.2 equiv.), HCOOH (50 equiv.), THF, 4 h, 80 °C. (iii) **Gru-II** (2 mol%), THF, 0.5 h, 40 °C, then **Gru-II** (2 mol%), HCOONa (0.2 equiv.), HCOOH (50 equiv.), THF, 4 h, 80 °C.

control offered by our transfer hydrogenation system. An equimolar mixture of **3a** and **3k** was subjected to the transfer hydrogenation process leading to complete reduction of the cyclopentene ring, with practically no reduction of a cyclohexene double bond under these conditions (Scheme 2).

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 the 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).

The precise details of the nature of catalytic species produced upon the action of HCOONa/HCOOH are unclear. It was reported that some Ru complexes can catalyse the decomposition of formic acid leading to the formation of CO_2 and ruthenium hydride species.[13] This suggests that entry into the catalytic cycle starts with the conversion of **Az-II** or **Gru-II** into Ru–hydride species, which act as the actual hydrogenation catalyst.[14,15] A similar mechanism was also suggested for other Ru-catalysed transfer hydrogenation reactions.[6] 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_8. Then the tube was closed and the reaction mixture was heated at 50 °C for 4 h. Then the tube was cooled down to room temperature and the NMR spectrum was recorded. A new signal with a chemical shift of −6.86 ppm appeared. This chemical shift is in the range characteristic for ruthenium hydride species.[16] 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 the alkene isomerisation process (C–C double bond migration)[17] that were decreasing with time (Scheme 4). Both these observations suggest the presence of

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Scheme 4 Incomplete isomerisation–hydrogenation of **3a**. Conditions: (i) **Gru-II** (2 mol%), NaH (0.2 equiv.), HCOOH (50 equiv.), THF. Conversion determined by ^{1}H NMR.

Ru hydride species during reduction with the Ru/HCOOH system described by us.

Conclusions

In conclusion, a mild protocol for transfer hydrogenation of alkenes has been demonstrated that exhibits a highly functional group tolerance and surprising selectivity. For a number of alkenes, the Ru/HCOOH system can be seen as a safe alternative to dangerous pressurized hydrogen gas. This method can also be coupled with olefin metathesis events, allowing for efficient one-pot sequences. Unlike other Ru-catalysed hydrogenation protocols, Ru/HCOOH allows for selective reduction of a given C–C double bond in the presence of relatively similar ones and is compatible with keto and enone functionalities that can be reduced by $NaBH_4$. Therefore the highly selective nature of this system provides a useful addition to the still expanding[6] repository of hydrogenation methods.

Experimental section

Procedure A. Reduction of C–C double bonds

Olefin (1 mmol) and 5 mL of anhydrous THF were placed under argon in a reaction tube. Next, catalyst **Gru-II** (2 mol%) was added to the resulting solution followed by the addition of HCOONa (0.2 mmol) and 98% HCOOH (50 mmol), and the reaction tube was closed. The reaction mixture was stirred for an appropriate period of time at 80 °C, then allowed to reach room temperature and poured into saturated aqueous solution of $NaHCO_3$ (ca. 30 mL). The aqueous layer was extracted with an appropriate organic solvent and the combined organic phases were washed with brine, dried over $MgSO_4$, 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**). A spectrally pure product was synthesized according to the procedure B without further purification (212 mg, 99%) using **3a** as a starting material and NaH instead of HCO_2Na. Analyses of the product were in accordance with the previously reported study.[18]

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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**). A spectrally pure product was synthesized according to the procedure A using commercially available substrate **1h** without further purification (161 mg, 83%). Analyses were in accordance with the previously reported study.[19]

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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) 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 complete 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 an appropriate period of time at 80 °C in a closed tube, then allowed to reach room temperature and poured into saturated aqueous solution of $NaHCO_3$ (ca. 30 mL). The aqueous layer was extracted with an appropriate organic solvent and the combined organic phases were washed with brine, dried over $MgSO_4$, 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**). The product was synthesized according to the procedure B using diene **1a** as a starting material and NaH instead of HCO_2Na. A spectrally pure product was isolated by extraction (214 mg, 99%). Analyses were in accordance with the previously reported study.[18]

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.7, 61.1, 60.4, 34.4, 25.4, 14.0.

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

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.9, 137.0, 132.8, 128.6, 128.6, 46.5, 30.1, 26.4.

Acknowledgements

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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 a gaseous mixture of H_2 and CO_2 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 ESI.‡

10 For representative examples of Ru-catalyzed transfer hydrogenation of ketones, see: (a) C. S. Cho, B. T. Kim, T.-J. Kim and S. C. Shim, *J. Org. Chem.*, 2001, **66**, 9020; (b) M. Babin, R. Clément, J. Gagnon and F.-G. Fontaine, *New J. Chem.*, 2012, **36**, 1548; (c) O. O. Kovalenko, H. Lundberg, D. Hübner and H. Adolfsson, *Eur. J. Org. Chem.*, 2014, 6639; (d) ref. 13a.

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

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