High Turnover Numbers with Ruthenium-Based Metathesis Catalysts

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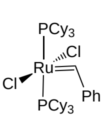
Abstract: Effective turnover numbers (TON's) and turnover frequencies (TOF's) of unprecedented magnitude have been obtained for the metathesis of various substrates in the presence of ruthenium-based catalysts, without the use of an additional solvent. For the self-metathesis of 1-octene, the 2nd generation Grubbs' catalyst $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2a**) ($IMesH_2 = 1,3$-dimesityl-4,5-dihydroimidazol-2-ylidene) gave TON's 5 times higher than those of the 1st generation catalyst $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**1**) while maintaining a high degree of selectivity for the formation of the product 7-tetradecene. Moreover, the catalyst $(IPrH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2b**), bearing the extremely bulky 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene ligand ($IPrH_2$), gave TON's 6 times higher (TON >640,000) and initial TOF's 20 times higher than those of **2a** at ambient temperature. At elevated temperatures, TOF's were twice as high and initial TOF's were 6 times as high for **2b** relative to **2a**, and with nearly 100% selectivity. Initial TOF's exceeding 3,800 s^{-1} could be achieved with **2b** at 60 °C. Under similar conditions, comparable TON's for the self-metathesis of *trans*-4-decene and methyl oleate, and the ring-closing metathesis of diethyl diallylmalonate were also obtained.

Keywords: catalytic activity; *N*-heterocyclic carbene (NHC) ligands; metathesis; P ligands; ruthenium

Introduction

The last few years have seen a significant resurgence in interest for olefin metathesis chemistry.[1] The renewed popularity can be largely attributed to the introduction of the well-defined, functional-group tolerant homogeneous ruthenium-derived catalyst $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**1**) developed by Grubbs and coworkers,[1a,1f] together with the molybdenum-based catalysts developed by Schrock.[1b,1e] Especially the ruthenium-derived catalyst systems have garnered much popularity with organic chemists for their ease of use (high air and moisture stability) and exceptional tolerance toward reactive functional groups. The presence of functional groups in substrates often thwarts traditional metathesis catalysts.[2] With the recent advent of the much more active 2nd generation ruthenium catalyst $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ ($IMesH_2 = 1,3$-dimesityl-4,5-dihydroimidazol-2-ylidene) (**2a**), incorporating a bulky neutral *N*-heterocyclic carbene (NHC) ligand,[3] the scope of olefin metathesis in organic synthesis has become even greater.

Although catalysts **1** and **2a** are powerful tools in organic synthetic strategies, the relatively high cost of ruthenium, coupled with the relatively high catalyst loading generally employed (typically 0.1–5 mol %),[4] render these systems disadvantageous for use in large-scale reactions. While these points are especially pertinent for potential industrial applications for these catalysts, they are also relevant when relatively inexpensive substrates are to be reacted. We have therefore focused our attention on the possibilities of utilizing catalysts **1** and **2a** for metathesis with the goal of maximizing the effective TON, a figure that is, surprisingly, rarely reported for homogeneous metathesis catalysts.



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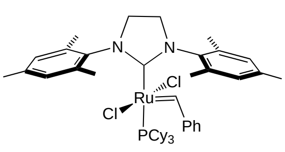
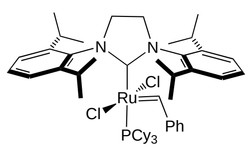
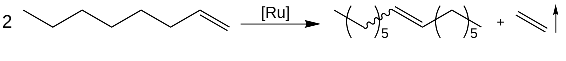


2a



2b

We chose 1-octene as a suitable substrate for initial study, since it is inexpensive and widely available. We now report results that reveal that, in fact, very low catalyst loadings (<1 ppm) can be successfully used in the self-metathesis of 1-octene, Equation (1).



(1)

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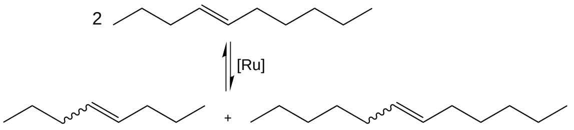
This success led us to also examine the metathesis of several other types of substrate, e.g., the self-metathesis of *trans*-4-decene, Equation (2), and methyl oleate, Equation (3), as well as the ring-closing metathesis of diethyl diallylmalonate, Equation (4).



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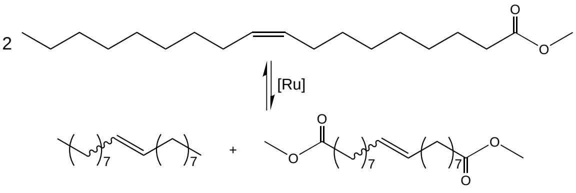

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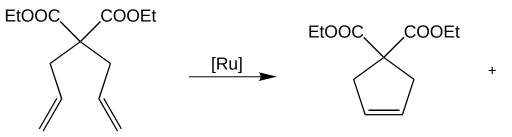

(4)

The synthesis, characterization and reactivity of the slightly modified 2nd generation Grubbs' catalyst **2b** is also reported, this compound giving metathesis reactivity differing significantly from that of either of the standard ruthenium catalysts **1** and **2a**.

Results and Discussion

Preparation and Properties of Catalyst 2b

In addition to exploring TON's for catalyst **2a**, we wondered if a further increase in the steric bulk of the NHC ligand might impart additional reactivity and, perhaps more importantly, longevity to the active catalyst. Because steric effects play an important role in ruthenium-based metathesis catalysts,[5] we prepared the 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazoline ($IPrH_2$) analogue of **2a**. The desired complex (**2b**), has also recently been prepared and characterized by Fürstner and coworkers,[6] although its catalytic activity has not yet been reported. We reasoned that the significant increase in steric bulk of $IPrH_2$ relative to $IMesH_2$, together with its superior electron-donating properties relative to the well-studied unsaturated analogue, IPr,[7] might give rise to a highly active metathesis initiator.[8]

Complex **2b** largely resembles its mesityl bearing analogue, with the exception of the ^{31}P NMR spectrum giving the PCy_3 signal slightly (2.4 ppm) up-field relative to that of **2a** at 28.1 ppm. No free PCy_3 was observed. Like **2a**, complex **2b** is brownish in appearance, and the ^1H NMR spectrum shows the diagnostic low-field benzylidene proton resonance at 19.77 ppm; **2a** shows the corresponding signal at 19.59 ppm. In contrast to the report by Fürstner,[6] we did not observe the formation of the dihydride complex $(PCy_3)_2Ru(H)_2(Cl)_2$ as a by-product in our (similar) synthetic procedure, and clean material could be directly isolated from the crude reaction residue by addition of methanol. However, we did notice that in pure samples of **2b** in C_6D_6, using standard (not airtight) NMR tubes, two additional singlet signals gradually appeared in the benzylidene region of the ^1H NMR spectrum at 18.95 and 17.82 ppm in a ~1:4 ratio. Full exposure to air led to a more rapid loss (minutes) of the benzylidene signal of the parent compound concomitant with growth of the new signals and the formation of tricyclohexylphosphine oxide (evidenced in the ^{31}P NMR spectrum). No other ^{31}P NMR signals were observed. Furthermore, addition of excess Cu(I)Cl directly to a C_6D_6 solution of **2b** gave identical spectra to the air-exposed sample, but without $O{=}PCy_3$ formation. Addition of PCy_3 to the Cu(I)Cl treated sample regenerates **2b** in good yield. From these experiments, we can tentatively conclude that the identity of at least one of these benzylidene-containing derivatives of **2b** is the 14-electron phosphine-dissociated species proposed in the catalytic cycle of olefin metathesis.[8,9] Noteworthy is that similar observations have recently been noted for $(IMesH_2)(PCy_3)(I)_2Ru{=}CHPh$, which in the ^1H NMR showed new benzylidene signals at similar positions, 18.14 and 17.17 ppm.[8] Attempts at the isolation of the phosphine-free derivative of **2b** from the Cu(I)Cl reaction, which appears to be quite stable in solution and the solid state, have been hampered by its high solubility in common organic solvents.

Metathesis of 1-Octene

Maximum Effective Turnover Number

Like all metathesis reactions, the metathesis of 1-octene is fully reversible. However, when the product ethene is allowed to escape, the reaction is rendered essentially irreversible, Equation (1). Metathesis catalysts also bring about the non-productive metathesis of the product 7-tetradecene. Because these metathesis events cannot be followed, the *total* turnover number for a given catalyst for the metathesis of 1-octene cannot be calculated with any degree of certainty. Moreover, because the active metathesis catalyst is the phosphine dissociated species,[8] whose concentration at any given

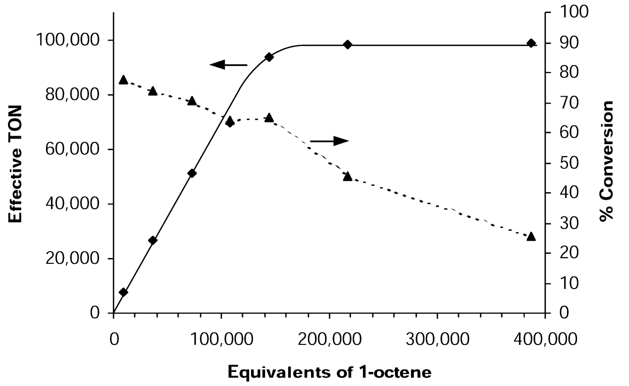

Figure 1. Effective TON and total conversion as a function of the number of equivalents of 1-octene for catalyst **2a** at 22 °C.

time cannot yet be accurately determined, the actual number of substrate molecules that have undergone metathesis by a particular ruthenium center also cannot be determined. Thus, the only meaningful figure that can be calculated with any degree of certainty is the *effective* TON, this being the total number of 1-octene molecules converted to metathesis products per molecule of the catalyst *precursor*.

When the maximum capabilities of the catalyst are reached, the effective TON should remain constant over a wide concentration range if the levels of impurities in the 1-octene that can poison or decompose the catalyst are sufficiently low. Accordingly, the quality of the 1-octene used for the various experiments was verified by testing the initiator **2a** over a wide range of dilutions, *viz.* a ratio of 9,600–386,000 equivalents of 1-octene to catalyst at 22 °C. Figure 1 graphically depicts the results of this study.

The maximum effective TON for catalyst **2a** is reached when about 95,000 molecules of substrate have been converted. This maximum TON can be achieved only when $>145{,}000$ equivalents of 1-octene are used, giving a $<65\%$ conversion. Additional 1-octene leads to lower conversions, but essentially the same TON's, while less 1-octene results in a higher conversion but overall a more inefficient use of the catalyst.

All subsequent metathesis experiments were carried out with an appropriate excess of substrate, to ensure the highest possible TON was reached in each case.

Selectivity

The selectivity for the formation of 7-tetradecene was generally very high ($>99\%$), but we did notice slightly lower selectivities ($\sim 95\%$) for the more concentrated mixtures. The major secondary product was determined by GC/MS to be tridecene, most probably formed from the cross-metathesis of 1-octene and 2-octene, the latter formed from C=C bond isomerization of the former. Trace amounts of dodecene arising from the self-metathesis of 2-octene were also detected. The data clearly show that the selectivity is dependent on reaction time, temperature and concentration. For example, in the case of catalyst **1**, when all metathesis activity had ceased, the remaining unreacted 1-octene was slowly isomerized giving almost equal parts of 1-, 2-, and 3-octene. This finding suggests that the decomposed metathesis initiator becomes a quite efficient double-bond isomerization catalyst. Therefore, if metathesis active species are still present late in the reaction, significant amounts of secondary products can be formed. While this process limits the potential recyclability of the remaining unreacted substrate, the judicious choice of catalyst loading, reaction time, and reaction temperature can certainly control, if not eliminate, the isomerization reaction.

Effect of Temperature

Next, metathesis experiments ranging from ambient conditions (22 °C) up to the boiling point of octene (122 °C) were carried out to determine the effect of temperature on TON's for the catalysts **1**, **2a**, and **2b** (Figure 2).

At room temperature (22 °C), catalyst **1** gives a maximum TON of 21,000. The 2nd generation catalysts, in particular **2b**, performed significantly better. As already mentioned above, catalyst **2a** gave an optimal TON of 95,000, while the TON achieved with catalyst **2b** exceeded 640,000. The reason for the appreciably higher TON of the catalyst **2b** relative to **2a** is not entirely clear, but could conceivably be attributed to a faster initiation rate (phosphine dissociation) together with a lower occurrence of non-productive metathesis of 7-tetradecene (*vide infra*) due to the increased steric bulk of the $IPrH_2$ ligand relative to $IMesH_2$. Faster initiation rates should give rise to higher TON's, which has recently been demonstrated for **2a** relative to the faster initiating triphenylphosphine analogue, $(IMesH_2)(PPh_3)(Cl)_2$

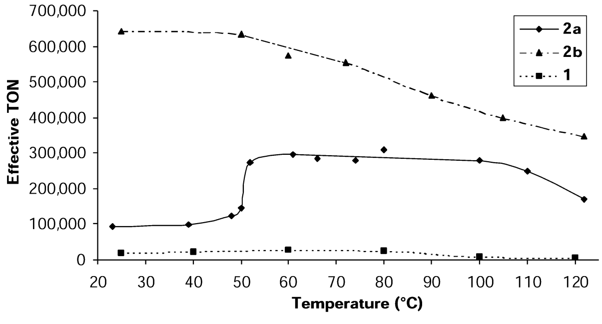

Figure 2. Effective TON as a function of temperature for catalysts **1**, **2a**, and **2b** for the metathesis of 1-octene. Reactions were deemed complete when no further metathesis activity was observed.

Ru=CHPh, the latter allowing much lower catalyst loadings.[8] The increased steric bulk of the $IPrH_2$ ligand might also impart additional protection of the ruthenium center, thereby slowing down the substrate independent decomposition pathways, although only very little is currently known about the formation and identity of the exhausted catalyst.

At higher temperatures, divergent results are observed. Catalyst **1** shows a steady increase in TON at elevated temperatures, up to 28,500 at 60 °C. Above 80 °C, a sharp drop-off in activity was noted; this presumably represents the decomposition temperature of the catalyst. Catalyst **2a** does not succumb appreciably to thermally-induced degradation until over 100 °C. From this point on a slight, but steady, decrease in TON was observed, ending with ~50% reduction in TON at 122 °C. Catalyst **2b** was found to be more thermally sensitive than **2a**, and shows an almost linear decrease in activity at temperatures higher than 50 °C. That said, even at 120 °C, the TON of **2b** is still higher than the maximum value recorded for **2a**.

Interestingly, the catalyst **2a** displays a very sudden increase in TON between 50 and 52 °C (Figure 2). Over this narrow temperature range the effective TON reproducibly doubled to ~300,000, and thereafter remained approximately constant up to ~100 °C. We also noticed a sharp decrease of 10–15% in selectivity above 50 °C after prolonged reaction times. Secondary metathesis products detected in these cases were nonene, decene, dodecene, and tridecene, with only the latter detected at any significant level at temperatures lower than 50 °C. Possibly, ~50 °C represents a threshold temperature for the more rapid initiation of **2a**, which then leads to higher TON's.[8] This phenomenon was not observed for **2b**, which maintained a relatively constant activity over a wide temperature range while retaining a very high degree of selectivity. The reason for the different behavior of the two 2nd generation catalysts at elevated temperatures is not entirely clear, but possibly involves the sterically induced faster initiation rate of **2b** relative to **2a**.

Effective Turnover Frequency

We also followed the rates of the metathesis reaction for the three catalysts under investigation at 22 and 60 °C. As for the determination of the TON, the unknown number of active catalytic species present in the solution means that the turnover frequency (TOF) of a particular molecule of catalyst cannot be determined. Thus, when measuring the rate profiles of the reactions, the values at any given time represent a TON averaged over all of the ruthenium species (those that are catalytically active, decomposed, and dormant) present in solution.

At 22 °C, catalyst **1** showed a low activity, and gave a maximum effective TOF of 2.4 s^{-1} after 5 min reaction time. As expected, catalyst **2a** gave a significantly higher maximum observed TOF of 4.2 s^{-1} at 45 min reaction time. Noteworthy is that an initiation period of ~30 min was observed for **2a**. In contrast, catalyst **2b** displayed no detectable initiation period, and a TOF more than 20 times higher (88 s^{-1}) than that of **2a** was measured after 15 minutes. Consequently, catalyst **2b** was completely exhausted after 7 h, while **2a** still showed some activity after 15 h.

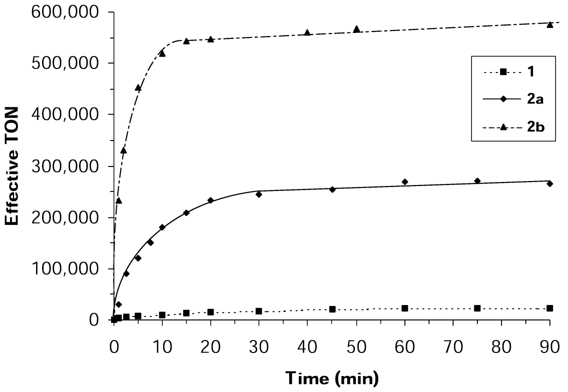

Figure 3. Effective TON as a function of time for catalysts **1**, **2a**, and **2b** in the metathesis of 1-octene at 60 °C, using 67,400, 718,000, and 1,154,000 equivalents of substrate, respectively.

Figure 3 shows the rates of metathesis at 60 °C. At this higher temperature, **2b** again displays much higher activity than both **1** and **2a**; a TOF of 3,800 s^{-1} was measured after 1 min reaction time for **2b**, while **1** and **2a** showed maximum TOF's of 60 and 670 s^{-1}, respectively.

Stereoselectivity

Finally, we investigated the stereochemistry of the 7-tetradecene isolated from 1-octene self-metathesis conducted at 22 and 60 °C. Because the *cis* and *trans* isomers of 7-tetradecene could not be readily separated by gas chromatography, the *cis*:*trans* ratio of the metathesis product was analyzed for the three catalysts by quantitative ^{13}C NMR experiments.[10] Table 1 shows a summary of the data.

The results are consistent with *cis*:*trans* ratios determined for a variety of reaction products involving

Table 1. *cis*:*trans* ratios of the 7-tetradecene formed from the metathesis of 1-octene by catalysts **1**, **2a**, and **2b**, at 22 and 60 °C.

Temperature [°C]	Catalyst	*cis:trans* ratio
22	**1**	40:60
	2a	16:84
	2b	16:84
60	**1**	40:60
	2a	22:78
	2b	22:78

Table 2. Self-metathesis of 1-octene, *trans*-4-decene and methyl oleate, and ring-closing metathesis of diethyl diallylmalonate at 55 °C in the presence of catalysts **1**, **2a**, and **2b**.[a] Neat solutions.

Substrate	Catalyst	Equivalents of Substrate	Total Conversion [%]	Selectivity [%]	Effective TON
1-Octene	**1**	104,000	27	>98	28,500
	2a	490,000	60	91	295,000
	2b	1,400,000	41	>98	630,000
trans-4-Decene	**1**	4,200	30	>98	1,250
	2a	1,200,000	48	>98	570,000
	2b	208,000	15	>98	31,000
Methyl oleate[b]	**1**	25,000	10	>98	2,500
	2a	990,000	45	91[d]	440,000
	2b	240,000	25	>98	46,000
Diethyl diallylmalonate[c]	**1**	50,000	16	>98	8,000
	2a	1,160,000	17	>98	200,000
	2b	960,000	25	>98	240,000

[a] Reaction time 24 h. Reactions were carried out over a wide catalyst concentration range. Highest values are given.

[b] Successful metathesis dependent on the batch of methyl oleate used; TON's $>100,000$ could be reproducibly obtained with **2a**.

[c] TON's and selectivities were calculated using an internal standard (nonane).

[d] Slightly lower TON's but with $>98\%$ selectivity could be obtained at 22 °C.

aliphatic olefin substrates metathesized by catalysts **1** and **2a**.[4b,4d,11] The differing steric influence of the NHC ligands in catalysts **2a** and **2b** does not contribute to the stereoselectivity of the catalysts, since identical data were obtained for the two systems.

Metathesis of Other Substrates

The high TON's described above for the metathesis of 1-octene led us to examine three other substrates: *trans*-4-decene, methyl oleate, and diethyl diallylmalonate, Equations (2)–(4). Methyl oleate and diethyl diallylmalonate are of particular interest since they contain ester groups that can decompose many traditional metathesis catalysts.[2] Table 2 summarizes the results obtained using the three initiators under investigation for both the self-metathesis of *trans*-4-decene, Equation (2), and methyl oleate, Equation (3), as well as the ring-closing metathesis (RCM) of diethyl diallylmalonate, Equation (4).

From the data it is clear that the very high TON's shown for catalysts **2a** and **2b** can be readily extended to include other substrates, notably those containing ester groups. Catalyst **1**, however, shows only moderate TON's for the other substrates. Especially, a clear drop-off in activity on going from terminal olefins to internal ones for catalyst **1** is evident. The result obtained for methyl oleate is consistent with the TON previously reported, while that for *trans*-4-decene was found to be much higher.[12]

As has been observed by Fürstner and coworkers,[6] different NHC ligands present in the 2nd generation metathesis catalysts can give quite different metathesis activity, depending on the substrate, and this was also the case with catalysts **2a** and **2b**. For both *trans*-4-decene and methyl oleate, catalyst **2a** gives, unexpectedly, TON's higher than those measured for 1-octene, while catalyst **2b** gives significantly lower values. We speculate that the bulkier $IPrH_2$ ligand in **2b** hinders the approach of the *internal* olefin molecules to the Ru center, resulting in lower TOF's and consequently lower TON's. Studies to give a more definitive insight into this somewhat surprising result are in progress.

For the RCM of diethyl diallylmalonate, high TON's could be obtained without any added solvent using catalyst **2a**.[13] This result sharply contrasts that of the seminal report by Grubbs, where a minimal catalyst loading of 0.05 mol % (2,000 equivalents of substrate) of **2a** was required to initiate the RCM of diethyl diallylmalonate using CH_2Cl_2 as solvent.[3] The improved efficacy of **2b** relative to **2a** for 1-octene metathesis does not fully translate to the ring-closing metathesis of diethyl diallymalonate, although **2b** did consistently give slightly improved (~20%) TON's relative to **2a**.

Conclusions

The TON's for the 1st generation Grubbs' catalyst **1** and the 2nd generation catalysts **2a** and **2b** have been determined covering a wide temperature range (22–122 °C) for the metathesis of 1-octene. The metathesis reactions examined proceeded smoothly in the absence of added solvent, this being especially noteworthy given current environmental concerns regarding solvent use.[14] The 2nd generation catalysts display much higher TON's than the 1st generation catalyst. Similarly high TON's could also be obtained for the metathesis of *trans*-4-decene, methyl oleate and diethyl diallylmalonate. These high TON's are, to the best of our knowledge, unprecedented for ruthenium-based metathesis catalysts. A maximum TON of 110,000 has been reported for the poorly defined catalyst produced *in situ* from a $RuBr_3 \cdot x\ H_2O/PCy_3$/2-butyne-1,4-diol diacetate/H_2 mixture.[15]

The results reported here strongly imply that the ruthenium-based catalysts are, in all likelihood, often being used well below their maximum capabilities in many metathesis reactions, with loadings of 0.1–5 mol % (20–1,000 equivalents of substrate) being the norm.[4] While from the present work it is clear that solvents are not required for metathesis, they are unavoidable for RCM of large rings (to circumvent undesirable intermolecular metathesis reactions),[16] and also for solid substrates. It is quite likely that the presence of relatively low levels of catalyst poisons in the substrate play an important role in catalyst decomposition when very low catalyst loadings are used. Minimization of this problem should be controllable by more careful purification of the substrate. Furthermore, catalyst **2a** shows an unanticipated performance jump at ~50 °C for the metathesis of 1-octene, which was not observed for catalysts **1** and **2b**. Given that metathesis reactions using ruthenium catalysts are generally conducted in refluxing CH_2Cl_2, better results might be anticipated when using **2a** if a higher boiling solvent coupled with a slightly higher reaction temperature is used.

The selectivity of the metathesis reaction was found to be highly dependent on the reaction conditions, but was generally excellent for all three catalysts, independent of the substrates tested. While turnover frequencies were only determined at two temperatures (22 and 60 °C), it is noteworthy that the rate of metathesis was found to be extremely rapid at 60 °C for the 2nd generation catalysts.

We are currently exploring additional reaction conditions to further optimize the effective TON for the metathesis of 1-octene and other substrates, together with investigations of additional 2nd generation Grubbs' catalysts bearing modified NHC ligands.

Experimental Section

General Remarks

All manipulations were carried out under an inert atmosphere of nitrogen on a vacuum line using standard Schlenk techniques. All solvents used were dried and distilled under nitrogen prior to use. The catalysts **1**[17] and **2a**,[3] and 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolinium chloride[18] were prepared following literature procedures. Potassium *tert*-pentoxide solution (1.7 M in toluene, Fluka) and octadecane (Sigma) were used as received. 1-Octene (98%, Aldrich) was passed through a column (20 cm × 1.5 cm) of neutral alumina (Acros, 50–200 μm), using 15 g of alumina per 100 mL of 1-octene. The column was attached to a Schlenk flask and elution of the octene was facilitated by use of a slight vacuum applied to the flask. The octene was then deoxygenated by a series of degassing (by evacuation of the flask), followed by filling with nitrogen. The required amount of octene was then immediately transferred by a N_2-flushed syringe to degassed Schlenk flasks in which the metathesis experiments were to be carried out. NMR spectra were recorded on a Varian Mercury 300 spectrometer, at 300.14, 75.48, and 121.50 MHz for the proton, carbon and phosphorus channels, respectively.

Complex 2b

Potassium *tert*-pentoxide solution (~1.7 M in toluene, 190 μL, 0.323 mmol) was added to a suspension of 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolinium chloride (0.135 g, 0.316 mmol) in hexanes (20 mL). The stirred mixture was subsequently placed in an oil bath at 50 °C and reacted for 5 min; the milky suspension rapidly became cloudy. The solution was then added (by way of a stainless steel cannula fitted with a filter) to catalyst **1** (0.200 g, 0.243 mmol) suspended in hexanes (20 mL). The combined solution was heated by oil bath at 50 °C for 30 min, resulting in a clear dark brown solution. The solvent was completely removed under vacuum and degassed methanol (20 mL) was added to the dark brown residue, producing a fine powder upon stirring (1 h). The solid was filtered under N_2, washed with methanol (4 × 15 mL), and finally dried under vacuum to give **2b** as a light brown powder; yield: 0.175 g (80%). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 28.1$; ^1H NMR (C_6D_6): $\delta = 19.77$ (s, 1H, Ru=C*H*Ph), 8.25 (br s, 1H, *ortho* C*H*), 7.23–7.12 (multiple peaks, 5H, aryl C*H*), 6.97 (t, 2H, *para* C*H*, $^3J_{HH} = 7.8$ Hz), 6.70 (s br, 2H, aryl C*H*), 4.19 (sept, 1H, $CH(CH_3)_2$, $^3J_{H,H} = 6.5$ Hz), 3.76 (t, 2H, CH_2CH_2, $^3J_{H,H} = 7.8$ Hz), 3.69 (t, 2H, CH_2CH_2, $^3J_{H,H} = 7.8$ Hz), 2.27 [s br, 1H, $CH(CH_3)_2$], 1.70–1.02 [multiple peaks, 45H, PCy_3 and $CH(CH_3)_2$]; $^{13}C\{^1H\}$ NMR: $\delta = 296.7$ (d, Ru=*C*HPh, $^2J_{C,P} = 8$ Hz), 222.24 [d, Ru-*C*(N)$_2$, $^2J_{C,P} = 80$ Hz], 151.5, 149.9, 147.3, 138.5, 136.3, 131.9, 130.6, 129.3, 124.8, 124.3, 55.2 (CH_2CH_2), 54.6 (CH_2CH_2), 32.6, 32.4, 29.9, 29.6, 28.5, 28.3, 28.2, 27.8, 27.1, 26.8, 24.2, 24.1; anal. calcd. for $C_{52}H_{77}N_2Cl_2PRu$: C 66.93, H 8.32, N 3.00%; found: C 66.84, H 8.44, N 2.94%.

Metathesis Experiments

In a typical experiment, between 10 and 60 mL (64–382 mmol) of 1-octene were used. Degassed octadecane (~5% of the volume of octene used), which is less volatile than any of the metathesis products, was used as an internal standard. To the solution was then added an accurately weighed sample (six-figure analytical balance) of solid catalyst, in the range of 0.25–2.0 mg. No additional solvents were added. In each case, the reaction vessel was allowed to vent to an oil bubbler. A constant slow stream of nitrogen ensured anaerobic conditions for the duration of the experiment. All reactions were thoroughly stirred by way of a magnetic stirrer bar. For the various temperature experiments, the reaction vessel was immersed in an oil bath and allowed to equilibrate to the desired temperature before introduction of the catalyst. The progress of the metathesis reactions was measured by GC/FID (Carlo Erba 8000 Top) equipped with a DB-5 (J&W Scientific) column. An error of ±5% was estimated for the analysis of a given metathesis reaction based on the reproducibility of data from duplicate and triplicate experiments. At higher temperatures (> 80 °C), severe effervescence arising from ethene production was often encountered, this unavoidably causing undesirable and uncontrollable cooling of the reaction mixtures and evaporation of the substrate; errors for these experiments are estimated at ± 5 – 10%.

For the metathesis of *trans*-4-decene (Fluka), methyl oleate (Aldrich), and diethyl diallylmalonate (Aldrich), the substrates were first passed through small columns of alumina ending with a plug of celite, and thoroughly degassed. Volumes of 1 mL of substrate were used for the reactions. Solutions of known concentration of the catalyst were prepared in 5 mL of hexanes for catalysts **2a** and **2b**, and 2 mL of benzene for catalyst **1**, and 10 – 50 µL quantities of these solutions were then introduced via N_2-flushed syringe to the preheated (55 °C) substrates. Final reaction compositions were determined in the same way as for 1-octene.

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References and Notes

[1] For recent reviews, see: a) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18 – 29; b) R. R. Schrock, *J. Chem. Soc. Dalton Trans.* **2001**, 2541 – 2550; c) A. Fürstner, *Angew. Chem. Int. Ed.* **2000**, *39*, 3012 – 3043; d) L. Yet, *Chem. Rev.* **2000**, *100*, 2963 – 3007; e) R. R. Schrock, *Tetrahedron* **1999**, *55*, 8141 – 8153; f) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413 – 4450; g) S. K. Armstrong, *J. Chem. Soc. Perkin Trans. 1* **1998**, 371 – 388; h) C. Pariya, K. N. Jayaprakash, A. Sarkar, *Coord. Chem. Rev.* **1998**, *168*, 1 – 48; i) M. Schuster, S. Blechert, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2036 – 2056.

[2] K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, London, **1997**.

[3] M. Scholl, S. Ding, C. W. Lee, Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953 – 956.

[4] For some recent examples, see: a) K. Grela, M. Bieniek, *Tetrahedron Lett.* **2001**, *42*, 6425 – 6428; b) C. Pietraszuk, H. Fischer, M. Kujawa, B. Marciniec, *Tetrahedron Lett.* **2001**, *42*, 1175 – 1178; c) J. A. Smulik, S. T. Diver, *Tetrahedron Lett.* **2001**, *42*, 171 – 174; d) F. C. Engelhardt, M. J. Schmitt, R. E. Taylor, *Org. Lett.* **2001**, *3*, 2209 – 2212; e) T.-L. Choi, A. K. Chatterjee, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2001**, *40*, 1277 – 1279; f) J. Louie, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2001**, *40*, 247 – 249; g) A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 3783 – 3784.

[5] L. Jafarpour, S. P. Nolan, *J. Organomet. Chem.* **2001**, *617 – 618*, 17 – 27.

[6] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236 – 3253.

[7] a) L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49 – 54; b) L. Jafarpour, H-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5414 – 5416; c) L. Jafarpour, J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 3760 – 3763.

[8] M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543 – 6554.

[9] M. S. Sanford, L. M. Henling, M. W. Day, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2000**, *39*, 3451 – 3453.

[10] Applicability of quantitative ^{13}C NMR for the determination of the stereochemistry of internal olefins was verified by integration of the olefinic region of the ^{13}C NMR spectra obtained for mixtures of *cis*- and *trans*-3-heptene (both commercially available) of known composition. For 7-tetradecene, chemical shift values are 130.0 and 130.5 ppm for the *cis* and *trans* olefinic carbons, respectively.

[11] C. W. Lee, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 2145 – 2147.

[12] W. Buchowicz, J. C. Mol, *J. Mol. Cat. A: Chem.* **1999**, *148*, 97 – 103.

[13] That no *inter*molecular metathesis occurred between the substrates was verified by use of an internal standard.

[14] A. D. Curzons, D. J. C. Constable, D. N. Mortimer, V. L. Cunningham, *Green Chem.* **2001**, *3*, 1 – 6.

[15] P. O. Nubel, C. L. Hunt, *J. Mol. Cat. A: Chem.* **1999**, *145*, 323 – 327.

[16] a) C. W. Lee, R. H. Grubbs, *J. Org. Chem.* **2001**, *66*, 7155 – 7158; b) C. W. Lee, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 2145 – 2147.

[17] P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039 – 2042.

[18] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, *55*, 14523 – 14534.