Looking for the Noncyclic(amino)(alkyl)carbene Ruthenium Catalyst for Ethenolysis of Ethyl Oleate: Selectivity Is on Target

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Supporting Information

ABSTRACT: A wide set of 65 diverse Ru metathesis catalysts was investigated in the ethenolysis reaction of biosourced ethyl oleate to allow the comparison between the catalyst structure and its activity and selectivity. Handling of the oleic substrate, weighing of the catalysts, and charging the reactor were done in air, with exclusion of a glovebox or Schlenk techniques. A catalyst bearing the unsymmetrical N-heterocyclic ligand featuring a thiophene fragment (Ru-63) was selected to offer the best combination between high selectivity and sufficient activity under conditions mimicking oil industry practice. A proof-of-concept large-scale ethenolysis experiment was also done with the selected catalyst to prove its high selectivity at the 1 L scale reaction with a 90% pure non-distilled substrate.

INTRODUCTION

The olefin cross-metathesis (CM) transformation of seed and algae oils has significant potential as a sustainable way to obtain a number of valuable products.¹ Although the existing technology already in use in a plant located in Gresik, Indonesia, and planned for a new facility in Lahad Datu, Malaysia, is based on the CM of a palm oil with 1-butene (butenolysis),² the alternative process of ethenolysis is seen to be preferred industrially as it produces a less complicated product mixture, containing a higher amount of valuable 9-decanoic acid 9-DA (1, Scheme 1).³ Therefore, ethenolysis of methyl oleate (2a)—the widely used model of natural fatty acid glycerol esters—became a widely studied transformation in the recent years.⁴ Many research groups tried to develop the optimal reaction conditions and find the best catalyst for this process. Initially, ethenolysis of fatty oils was carried out with in situ formed catalytic systems, for example, WCl₆/SnMe₄.⁵ The more recent studies are however concentrating on well-defined Mo, W, or Ru catalysts.⁶ Because of their higher air and moisture stability, ruthenium complexes seem to be the best choice for the industrially effective ethenolysis of fatty esters.⁷

Unfortunately, as compared with butenolysis, in the ethenolysis of 2a, much lower turnover numbers (TONs) of only 2000−5000 were achieved with the standard Ru metathesis catalysts, although purified substrates and anaerobic conditions have been used.⁸ The reaction selectivity is also an issue, and although the first-generation Grubbs catalyst ((PCy₃)₂(Cl)₂RuCHPh) shows high selectivity for ethenolysis...
(though it is very short-living under the reaction conditions), the second-generation catalysts are significantly less selective because of their propensity for self-metathesis reactions. The reason why ethenolysis is so problematic lies in general low stability of propagating methyldiene ([Ru]=CH₂) species, a feature that makes most of the standard first- and second-generation Ru metathesis catalysts decompose very quickly in the presence of ethylene. Until now, the most promising results have been accomplished with Ru catalysts bearing so-called cyclic (amino)(alkyl)carbene (CAAC) ligands. Grubbs showed that with these catalysts, an impressive 180 000 TON can be achieved if ethylene of 99.95% purity is used and the reaction is conducted in a glovebox. The use of an expensive ultrahigh grade ethylene (99.995%) led to even higher 340 000 TON. In 2013, Shi et al. showed that CAAC catalysts can work even outside a glovebox (26 000 TON); however, 2a of 99% purity and vacuum-dried vessels (like in a Schlenk technique) were used. Recently, Skowerski reported up to 94 000 TON with a tailored CAAC catalyst, indicating that oleic acid used for the preparation of 2a was crystallized several times to remove other fatty acids, and ethylene of 99.99% purity was used. The above results (26 000–340 000 TON) are impressive and leave practically no room for further competition. However, after talks with technologists from a number of oil companies, we decided to focus more on the practicability issues, in order to consolidate the potential of modern metathesis catalysts in biomass conversion under practical oil industry conditions (vide infra, Scheme 2).

**Scheme 2. Ethenolysis of Ethyl Oleate (2b) Constraints**

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**RESULTS AND DISCUSSION**

Herein, we report our efforts to find an optimal catalyst structure and conditions for a practical ethenolysis of oleic ester (2b, Scheme 2). Our industrial partner in this study, Skotan S.A., imposed strict guidelines to make the ethenolysis process viable under conditions typically reachable in the oil industry, such as (i) complete banishment of a glovebox or Schlenk techniques as the above-mentioned techniques are impractical in industrial context, (ii) reaction setup, catalyst handling, and the reactor loading must be done possibly in air, with only an exceptional use of a protective atmosphere, (iii) use of ethylene grade 3.0 (99.9%) but not higher, and (iv) the oleic ester substrate should be of practical purity (90–95%) rather than of high (“research”) purity. Because of patent limitations, we were in addition asked to focus on non-CAAC catalysts. Such strict conditions made this task quite challenging; however, we hoped that perhaps by choice of the right Ru catalyst we can make it possible. On the basis of the results of Grubbs et al. on applications of Ru benzylidene complexes bearing unsymmetrical N-heterocyclic ligands (uNHCS) in ethenolysis of 2a, where relatively high TON of 5070 and excellent selectivity were achieved, we decided to screen a number of NHC and uNHC-bearing systems known in the literature, which were prepared in our laboratories. The Grubbs’ crucial observation that the uNHC complexes exhibit longer lifetimes in metathesis reactions, presumably as a result of the better stability of their methyldienes, was in line with our results on the application of some uNHC-bearing catalysts that exhibited outstanding selectivity in challenging self-CM and in a high-concentration macrocyclization via RCM (Ring-Closing Metathesis). Of note, the high selectivity of the ethenolysis step was the key factor requested by our industrial partner to make the whole process cost-efficient. This selectivity is defined as the proportion between the expected products (1b and 3) and the self-CM (sometimes referred to as “homodimerization”) products 4b and 5 (Scheme 2). As the planned ethenolysis process will not be run at full conversion, some amounts of isomerized (E/Z)-2b will be present in the reaction mixture as well (Scheme 2) and perhaps recycled (this was, however, not a goal of the present study).

On the basis of the previous results described in the patent and scientific literature and some preliminary in-house tests, we defined the starting condition to perform ethenolysis [catalyst loading 500 ppm; ethylene pressure 10 bar; temperature 50 °C; reaction time 3 h; and reaction scale 15 mmol (4.66 g of 2b)]. Distilled ethyl oleate of 95% purity was prepared from inexpensive technical-grade oleic acid and renewable bioethanol and stored over alumina (1 activity, neutral, 70–230 mesh, Merck) prior to use. The rationale behind using ethyl ester 2b, instead of more popular methyl ester 2a, was the availability of ethanol as a stream from other production activities. In addition, as we learned during distillation tests, the higher boiling point difference between 3 and 2b (the ethyl ester has a higher boiling point as compared with 2a) allowed for easier separation of these two products and led to more pure fractions even after single distillation (see the Supporting Information for more details). For the planned wide-screening tests, we selected a rather broad set of Ru complexes (Figure 1), composed of various types of compounds, and not excluding the catalysts tailored for specific applications, such as polymerization (Ru–28–Ru–29, Ru–34–Ru–35), as well as polar (Ru–38) or even chiral (Ru–27) Ru complexes, in order not to overlook a potential hit. The other rationale behind selecting such a heterogeneous set of complexes was to find the relationships between the structures of such diverse complexes and the conversion and selectivity exhibited by them in the ethenolysis reaction performed (Figure 1 and Table 1). It should be noted that although we always observed in the postreaction mixtures the undesired diethyl 9-octadecene-1,18-dioate and 9-octadecene (4b and 5), the amount of them was cleanly related to the catalyst used. The smallest amount of these self-CM products was observed for reactions with first-generation ruthenium catalysts of Grubbs, Hoveyda–Grubbs, and indenylidene type (Table 1, Ru-1 to Ru-4). In all these cases, the sum of 4b and 5 was below 4%. The first-generation phosphine-based complexes showed quite satisfactory conversion of ethyl oleate (55–65%); however, the yield of ethenolysis products (1-decene and ethyl decenoate) was reduced by the presence of double bond migration products in the reaction mixture (9–23%), making the product isolation quite complicated. The second-generation complexes in general exhibited a greater activity in both of these reactions, i.e., in the expected CM with ethylene and...
unfortunately also in the self-CM process, leading to byproducts 4b and 5.

The results presented in Table 1 cleanly showed that especially the symmetrical NHC-based catalysts (Ru-5−Ru-16, Ru-21−Ru-25, Ru-31, and Ru-36−Ru-38) gave more self-CM products than the first-generation complexes. Exhibiting selectivity between 3 and 80%, these NHC-bearing complexes cannot compete with the CAAC catalysts Ru-18−Ru-20, used as a benchmark in our study (selectivity 83−99%). The only exception was the SIPr catalyst Ru-17 displaying a comparable selectivity of 89% and good activity. Nonetheless, all symmetrical SIMes NHC-bearing catalyst, the third-generation complex (Ru-28), chiral Ru-27, and other specialized complexes appeared to be less advantageous in the ethenolysis as compared with CAAC ones (Table 1). Also, variation of the phosphine ligands does not bring to visible improvements. From the results presented in Table 1, some general trends can be observed:

- Hoveyda-type SIMes catalysts substituted in the benzene ring of the benzylidene moiety. The best results were

Figure 1. Ruthenium-based metathesis catalysts used in this study.
observed in the case of the NHCOCF₃ group (Ru-9). The introduction of other electron-withdrawing groups (EWGs) led to lowering the selectivity (Ru-11, Ru-12). The NO₂ substituent, one of the strongest EWGs, caused even greater decrease in selectivity (from 43% for Ru-5 to barely 3% for Ru-7). The other substituents (Me or OMe in Ru-15, Ru-24, Ru-25) do not cause any effect considerably.

- Hoveyda-type catalysts substituted in the alkoxy part of the benzylidene moiety. In our hands, modification of this part of a molecule did not add any improvement to the conversion and selectivity (see Ru-21, Ru-23 to Ru-25). The drop of selectivity in the case of Ru-37 and Ru-39 is similar to the one observed for the EWG-activated catalysts described above.

- Modification of the NHC backbone while keeping N-aryl substituents the same. In general, no positive effect was observed for catalysts Ru-26, Ru-40 to Ru-54, which all showed inclination toward self-CM even in the presence of ethylene. As this class of complexes is structurally diverse, no precise conclusions can be drawn.

- SIMes versus SIPr NHC ligands. It was observed that the complexes with the SIPr ligand (a ligand with 2,6-diisopropylphenyl N-substituents) are more selective toward ethenolysis products (1b and 3) and gave better yields than their SIMes analogues.

- Replacement of chlorine with iodine. A significant increase of the selectivity almost in each case was observed. The same observation can be extracted from the studies made by Pederson.17 For a prototypical Hoveyda–Grubbs second-generation catalyst, the Cl into I exchange seems to be a quick and simple method for making ethenolysis of 2b more effective. In this case, we observed a prominent growth in selectivity from 43% (Ru-5) to 76% (Ru-6), while maintaining a quite good conversion (77%). However, in some cases (e.g., Ru-18 vs Ru-19), this modification was associated with a visible decrease of the catalyst activity.

"Reaction conditions: catalyst loading 500 ppm; ethylene pressure 10 bar; ethylene purity 99.9% (3.0 grade); temperature 50 °C; time 3 h (in parenthesis time 6 h). "Determined by GC using tetradeacne as the internal standard and calibration curves (for ethyl oleate, tetradecane, and all the metathesis products 1b, 3, 4b, 5). "Conversion = 100 × (final moles of 2b/initial moles of 2b). "Yield of 3 = 100 × (moles of 3/initial moles of 2b). "Yield of 1b = 100 × (moles of 1b/initial moles of 2b). "Selectivity = 100 × (moles of 1b + moles of 3) / [(moles of 1b + moles of 3) + 2 × (moles of 4b + moles of 5)].

Table 1. Ethenolysis of Ethyl Oleate

| catalyst | conversion (%) | yield [%] of 3 | yield [%] of 1b | selectivity (%) |
|----------|----------------|---------------|----------------|----------------|
| Ru-1     | 57             | 25 (29)       | 32 (42)        | 93             |
| Ru-2     | 67             | 44 (48)       | 51 (57)        | 93             |
| Ru-3     | 52             | 43 (47)       | 48 (53)        | 98             |
| Ru-4     | 65             | 31 (39)       | 38 (47)        | 90             |
| Ru-5     | 71             | 20            | 25             | 43             |
| Ru-6     | 77             | 41            | 55             | 76             |
| Ru-7     | 56             | 1             | 2              | 3              |
| Ru-8     | 38             | 17            | 22             | 40             |
| Ru-9     | 79             | 47            | 58             | 70             |
| Ru-10    | 59             | 31            | 43             | 73             |
| Ru-11    | 53             | 9             | 11             | 17             |
| Ru-12    | 56             | 8             | 9              | 15             |
| Ru-13    | 80             | 51            | 57             | 72             |
| Ru-14    | 74             | 35            | 45             | 78             |
| Ru-15    | 77             | 41            | 47             | 66             |
| Ru-16    | 84             | 43            | 52             | 74             |
| Ru-17    | 70             | 46            | 60             | 89             |
| Ru-18    | 84             | 62            | 74             | 83             |
| Ru-19    | 42             | 39            | 42             | 99             |
| Ru-20    | 72             | 47            | 56             | 88             |
| Ru-21    | 57             | 12            | 14             | 26             |
| Ru-22    | 59             | 10            | 12             | 21             |
| Ru-23    | 81             | 10            | 19             | 43             |
| Ru-24    | 82             | 36            | 45             | 69             |
| Ru-25    | 74             | 29            | 35             | 54             |
| Ru-26    | 17             | 2             | 2              | 22             |
| Ru-27    | 39             | 13            | 16             | 38             |
| Ru-28    | 54             | 2             | 2              | 4              |
| Ru-29    | 40             | 6             | 7              | 23             |
| Ru-30    | 81             | 14            | 24             | 49             |
| Ru-31    | 60             | 14            | 15             | 28             |
| Ru-32    | 48             | 5             | 6              | 13             |
| Ru-33    | 58             | 17            | 20             | 32             |
| Ru-34    | 64             | 16            | 19             | 33             |
| Ru-35    | 38             | 5             | 5              | 17             |
| Ru-36    | 70             | 23            | 27             | 45             |
| Ru-37    | 54             | 4             | 5              | 8              |
| Ru-38    | 23             | 18            | 21             | 80             |
Until now, the obtained results were rather disheartening, clearly showing that CAAC catalysts exhibit the best combination of activity and selectivity, and none of the complexes tested until now can compete with them.

The Grubbs’ crucial observation that Ru complexes with two different N-substituents at the NHC moiety can exhibit up to 5070 TON in a glovebox-type ethenolysis of 2a \(^{2a}\) prompted us to focus on similar complexes that were at that time under development in our laboratories. To do so, 11 different ruthenium catalysts bearing uNHC ligands were screened at the same conditions as previously described (Table 1, Ru-55–Ru-65). We were pleased to find that most of the studied complexes were able to secure good conversion and high selectivity of the process, and only in the case of nonstable \(^{15}\)e pyrrole-substituted complex Ru-65, the conversion was low (17%); however, the selectivity was still high (91%). Interestingly, easy to be synthesized N-benzyl-substituted complexes (Ru-55 to Ru-60) \(^{15a,b,c,d}\) also revealed high efficiency toward ethenolysis of ethyl oleate (Table 1). The most promising catalyst was however the thiophene-substituted analogue of the above (Ru-63). \(^{15f}\) In this case, we observed the highest selectivity (90%) toward the desired ethenolysis products 1b and 3. This selectivity level is comparable with the selectivity observed for the best CAAC-type complexes \(^{1}\) and was fully satisfactory for the industrial partner. The halide exchange reaction led to the complex Ru-64 of even more increased selectivity (to 99%), which was however paired with the decreased catalytic activity (conversion of 42%).

Having selected the set of uNHC complexes characterized by the excellent selectivity and good activity, a brief optimization of conditions was made (Table 2). In order to observe potential initial choice of reaction time and pressure was close to the optimal, as 1 h reaction time was visibly insufficient to ensure the high conversion, and at the same time, decrease in the pressure of ethylene caused erosion of selectivity or conversion, or both (Table 2). The best results were observed when the reaction was conducted for a longer time (3–6 h) and at higher ethylene pressure (20 bar) to give—for the winning complex Ru-63 at 200 ppm loading—conversion above 70% and selectivity of 93% (Table 2).

The final and last step in our study was to try reducing the catalyst loading, as this can affect favorably the cost-effective parameter of the planned process. Keeping in mind that the use of glovebox or Schlenk techniques is not permitted, so using the same conditions and reagents’ purity we run the ethenolysis reaction with 200, 100, 50, and 25 ppm of the catalyst Ru-63 (Table 3). The results showed that the satisfactory conversion can be achieved for a catalyst loading equal to 100 ppm, whereas 2b handling and an autoclave charging were made in air. Although the main goal of this work was to find the most robust and selective catalyst within a set of structurally diverse Ru complexes, we decided in addition to test the selected catalyst Ru-63 in an ethenolysis of 2b at a larger scale. In this experiment, we used nondistilled ethyl oleate of 90% gas chromatography (GC) purity. This substrate was made by the esterification of crude oleic acid, and instead of distillation, it was purified by the treatment with Magnesol (5 wt %), activated alumina (2.5 wt %), and degassed in vacuo (for a detailed procedure, see the Supporting Information). Such obtained nondistilled ethyl oleate can be stored for prolonged periods of time. Immediately before the ethenolysis reaction, the required amount of 2b was again degassed under vacuum at 50 °C for 0.5 h.

The proof-of-concept large-scale ethenolysis was done as follows (Scheme 3): a 2 L reactor was evacuated under vacuum and a precooled \(^{1}\) mixture of substrate 2b (1 L) and catalyst Ru-63 (150 ppm) \(^{3}\) was sucked into the reactor. The reaction was run at 50 °C under the ethylene pressure of 20 bar. Ethenolysis was carried out for 2 h, ethylene was removed from the reactor, and then the reactor was flushed twice with a nonflammable gas. An aliquot of the reaction mixture was analyzed by GC, which showed the formation of only small amounts of unwanted “homodimers” 4b (1.5%) and 5 (1.1%), whereas the conversion of 2b was 56%. \(^{19}\) The reaction mixture was then transferred into a vessel containing 660 ppm of the SnatchCat metal scavenger, \(^{18}\) 1,4-bis(3-isocyanopropyl)piperazine 6 (4.4 equiv relative to the

Table 2. Optimization of Ethenolysis Conditions \(^a\)

| conditions time (h)/temp. (°C)/pressure (bar) | Ru-24 conversion (%) | Ru-59 conversion (%) | Ru-63 conversion (%) |
|---------------------------------------------|-----------------------|----------------------|---------------------|
| 3/30/10                                    | 51 (38)               | 52 (78)              | 58 (91)             |
| 3/50/10                                    | 58 (45)               | 63 (84)              | 50 (90)             |
| 3/80/10                                    | 65 (43)               | 60 (73)              | 45 (89)             |
| 1/50/10                                    | 34 (14)               | 50 (22)              | 49 (91)             |
| 6/50/10                                    | 68 (49)               | 62 (78)              | 66 (89)             |
| 3/50/2                                    | 63 (26)               | 51 (54)              | 31 (75)             |
| 3/50/20                                   | 77 (68)               | 54 (87)              | 71 (93)             |

\(^a\)Catalyst loading 200 ppm; ethylene purity 99.9% (3.0 grade); time (h)/temperature (°C)/pressure (bar). \(^b\)Determined by GC using tetradecane as the internal standard with calibration curves (for ethyl oleate, tetradecane, and all the metathesis products 1b, 3, 4b, 5). \(^c\)Conversion = 100 − 100 × (final moles of 2b/initial moles of 2b). \(^d\)Selectivity = 100 × (moles of 1b + moles of 3)/[(moles of 1b + moles of 3) + 2 × (moles of 4b + moles of 5)]. \(^\text{TON}^e\) = yield × (initial moles of 1b/moles of the catalyst)/100; TONs are calculated for the time of 3 h.
catalyst), and directly submitted to fractional distillation under reduced pressure. The relatively big difference between the boiling points of the products allowed to obtain practically pure fractions of 1b (33% yield) and 3 (30% yield) after just single distillation event, and the waste interfraction was relatively small (see the Supporting Information).

CONCLUSIONS

The ethenolysis reaction of ethyl oleate has been performed to allow the comparison between the structure of various catalysts and their activity and selectivity under “practical” conditions. The handling of the oleic substrate and weighing of the catalysts were done in air, with exclusion of a glovebox or Schlenk techniques. A wide set of 65 diverse Ru metathesis catalysts was investigated under such conditions that mimic the oil industry practice, allowing for the selection of the most robust and selective system, being a Ru catalyst bearing the uNHC featuring a thiophene fragment (Ru-63). In addition, a proof-of-concept larger-scale ethenolysis experiment was done with such a selected catalyst. Although this preliminary experiment at only 1 L scale cannot be used to assess the economic validity of the commercial-scale ethenolysis process, it shows that by selecting a robust and selective catalyst the amount of unwanted byproducts can be kept minimal. Research on improving the ethenolysis efficiency with the catalyst Ru-63 and/or on recycling of unreacted (E/Z)-2b will be continued in due time. In summary, we believe that the present results define a starting point for future scale-up studies, which hopefully allow finally for a green transformation of various types of biomass into the valuable chemical, 9-decenoic acid (9-DA), by ethenolysis.

EXPERIMENTAL SECTION

General Information. Technical oleic acid (purity 90%) was purchased from Sigma-Aldrich. Ethylene gas 3.0 grade (99.9%) was purchased from Linde (3.0 grade; O2 <30 ppm, N2 < 150 ppm, C2H6 <1800 ppm). Tetradeacne (purity 99%) was purchased from Linegal Chemicals, ethyl-vinyl ether (purity 99%) was purchased from Roth, and SnatchCat scavenger (6) was obtained from Sigma-Aldrich. NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. NMR chemical shifts are reported in parts per million downfield from the solvent residual peak (7.26 and 77.16 ppm for 1H and 13C in CDCl3). Deuterated chloroform was purchased from Sigma-Aldrich, stored over molecular sieves, and used without further purification. Calibration curves and GC analyses during the screening stage (Tables 1–3) were performed by means of a PerkinElmer Clarus 580 chromatograph with a flame ionization detector and a GL Sciences InertCap SMS/Sil Capillary Column (inner diameter 0.25 mm, length 30 m, d.0.50 μm). Tetradeacne was used as an internal standard in all screening low-scale experiments. Calibration curves were generated for ethyl oleate, tetradeacne, and all the metathesis products 1b, 3, 4b, 5. GC–MS analyses were performed by means of a PerkinElmer Clarus 680 chromatograph with a Mass Spectrometer Clarus SQ 8C detector and GL Sciences InertCap SMS/Sil Capillary Column (inner diameter 0.25 mm, length 30 m, d.0.50 μm). The large-scale reaction mixture (Scheme 3) and distillation fractions were analyzed with a PerkinElmer GC unit, with a GL Sciences InertCap SMS/NI (inner diameter 0.25 mm, length 30 m) column, using the following method: initial temperature 145°C−0.1 min−9°C/min to 180°C−0.1 min−20°C/min to 305°C−2 min. The qualitative analysis of fractions was made using GCMS-QP2010 Ultra Shimadzu Zebro ZB-5MSi GC–MS hardware.

Ethenolysis Tests Made in Small Scale (15 mmol, 4.66 g of 2b)—Tables 1–3. All catalysts, ethyl oleate (for purification details, see the Supporting Information), and tetradeacne (an internal standard) were weighed and handled in air. Armar and Roth autoclaves used in this stage (Tables 1–3) were charged with the reactants in air. Catalysts’ stock solution were made in air using dry dichloromethane (DCM; from the MB SPS-800 solvent purification system). A solution of a catalyst (500, 200, 100, 50, and 25 ppm) in DCM (100 μL) was added to a mixture of ethyl oleate (4.66 g, 15.0 mmol) and tetradeacne (0.61 g, 3.05 mmol) placed in a glass vessel containing a magnetic stir bar. The vessel was immediately installed into an autoclave, which was then flushed three times with ethylene (2 or 10 or 20 bar). The mixture was stirred at the temperature equal to 30°C or 50°C or 80°C for 1, 3, or 6 h. After that, a sample of the reaction mixture was collected (1 mL) and immediately quenched with ethyl vinyl ether (4 mL, used as 2 M solution in DCM). Next, an aliquot (0.2 mL) was taken from this mixture and diluted with 0.8 mL of DCM. Such obtained solution was analyzed by GC. Conversion was calculated using the internal standard and calibration curves.

Large-Scale (1 L) Ethenolysis and Distillation (Schemes 3 and S2). Before each reaction of ethenolysis, a 2 L Büchi autoclave used in the large-scale experiments was washed with one portion of DCM (800 mL), two portions of acetone (700 mL each), and one portion of toluene (700 mL), with stirring for 5 min (800 rpm) each time. Then the reactor was dried under reduced pressure (1–5 mbar) with the jacket heated to the temperature of 65°C. A catalyst stock solution was prepared as follows: the solid catalyst was weighed in air into a 25 mL flask, which was then flushed with argon, and the catalyst was dissolved in 14 mL of dry toluene (distilled over Na). To a vacuum-heated 2 L flask substrate, 2b (870 g, 1000 mL) for purification details, see the Supporting Information) was added. The flask was cooled to 0°C, and the catalyst solution (10 mL, 150 ppm) was added with stirring. The ethenolysis reactor together with its gas supply line was connected to vacuum, and the substrate—catalyst mixture was vacuum-sucked into the reactor (reactor’s jacket temperature was set equal to the reaction temperature), whereas the stirring speed was set at 600
rpm. Next, ethylene was added to reach the set pressure, and the reaction was carried out for 2 h. After this, ethylene gas was removed from the reactor, which was flushed twice with argon, to remove any traces of the flammable ethylene. A tiny sample of the reaction mixture was subjected to GC, whereas the rest was transferred into a vessel containing 660 ppm of 1,4-bis(3-isocyanopropyl)piperazine 6 (SnatchCat) (4.4 equiv relative to the catalyst). Directly after quenching, the reaction mixture was subjected to fractional distillation. A 1 L flask containing 600 g of the postreaction mixture was connected to a glass distillation equipment containing a 44.5 cm long jacketed rectifying column. The entire distillation was carried out at a pressure of 1–2 mbar. Three fractions were collected: 1-decene fraction (purity 96%, 122.0 g), a mixed fraction containing 1-decene together with 9-DA ethyl ester (3–38%, 1b—49%, 3.1 g), and the fraction of 9-DA ethyl ester 1b (purity 97%, 179.5 g).

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Although no industrial production utilizing well-defined molybdenum or tungsten alkenylidenes has yet been disclosed, these catalysts offer a number of advantages, such as modularity, low propensity towards C=C double bond isomerization and high selectivity in ethenolysis (see ref 3), to list only a few. Recently some propensity towards C=C double bond isomerization and high selectivity in ethenolysis (see ref 3), to list only a few. Recently some.