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Cyclic Alkyl Amino Carbene (CAAC) Ruthenium Complexes as Remarkably Active Catalysts for Ethenolysis**

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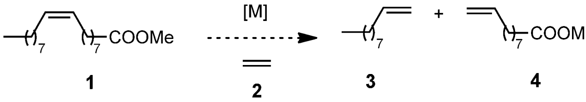
Abstract: *An expanded family of ruthenium-based metathesis catalysts bearing cyclic alkyl amino carbene (CAAC) ligands was prepared. These catalysts exhibited exceptional activity in the ethenolysis of the seed-oil derivative methyl oleate. In many cases, catalyst turnover numbers (TONs) of more than 100 000 were achieved, at a catalyst loading of only 3 ppm. Remarkably, the most active catalyst system was able to achieve a TON of 340 000, at a catalyst loading of only 1 ppm. This is the first time a series of metathesis catalysts has exhibited such high performance in cross-metathesis reactions employing ethylene gas, with activities sufficient to render ethenolysis applicable to the industrial-scale production of linear α-olefins (LAOs) and other terminal-olefin products.*

The transformation of small-molecule chemical feedstocks to high-value chemicals has been a long-standing challenge that has received a significant resurgence of interest in the chemical sciences. This is a result of recently introduced programs promoting the use of "greener" chemistry practices, as well as the rising costs associated with the production of fine chemicals from petrochemicals. Consequently, the ability to access high-demand products from renewable sources such as oleochemicals presents a cost-effective and environmentally friendly alternative.[1]

Olefin-metathesis reactions, such as cross-metathesis (CM), ring-closing metathesis (RCM), and ring-opening metathesis polymerization (ROMP), all of which generate a new internal olefin, have enjoyed widespread popularity in both academic and industrial settings as a result of their general applicability, ease of use, and affordable costs.[2] Ruthenium-based metathesis catalysts are ideal for such transformations because of their generally robust nature, which enables handling in air and imparts good tolerance to a variety of functional groups and trace impurities. All of these are necessary prerequisites when subjected to raw materials or biomass.

Many renewable or bio-based materials, such as fatty acids originating from seed oils and their derivatives, contain at least one carbon–carbon double bond, which provides a synthetic handle for derivatization by olefin-metathesis catalysts. The CM reaction with ethylene (**2**), commonly referred to as ethenolysis, has significant potential as a clean, scalable, and sustainable solution for the production of linear α-olefins (LAOs; e.g. **3** and **4**) from the natural oils found in oleochemicals such as methyl oleate (MO, **1**; Scheme 1).



Scheme 1. Ethenolysis of the seed-oil derivative methyl oleate (**1**).

LAOs are direct precursors to a variety of commodity chemicals with applications as fuels, surfactants, lubricants, waxes, perfumes, antimicrobial agents, and thermoplastics. In addition, LAOs can be rapidly elaborated to more complex products, such as agrochemicals, insect pheromones, and pharmaceuticals.[3]

The production of terminal olefins through the ethenolysis of seed-oil derivatives using metathesis catalysts has been previously demonstrated. However, the high catalyst loadings required (10–100 ppm) to achieve an acceptable yield of terminal olefins render these reported procedures cost-prohibitive on an industrial scale.[4–6] In general, catalyst turnover numbers (TONs) of at least 35 000 and 50 000 are recommended in the manufacturing of specialty and commodity chemicals, respectively.[4] In the ethenolysis of the benchmark substrate MO (**1**), standard ruthenium-based metathesis catalysts, such as **5**–**8** (Figure 1), afforded TONs of only 2000–5000. This result stands in contrast to the extremely high activity normally exhibited by these catalysts in CM with terminal or internal olefins. For example, TONs as

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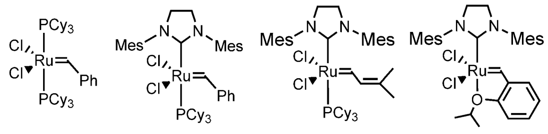


5 **6** **7** **8**

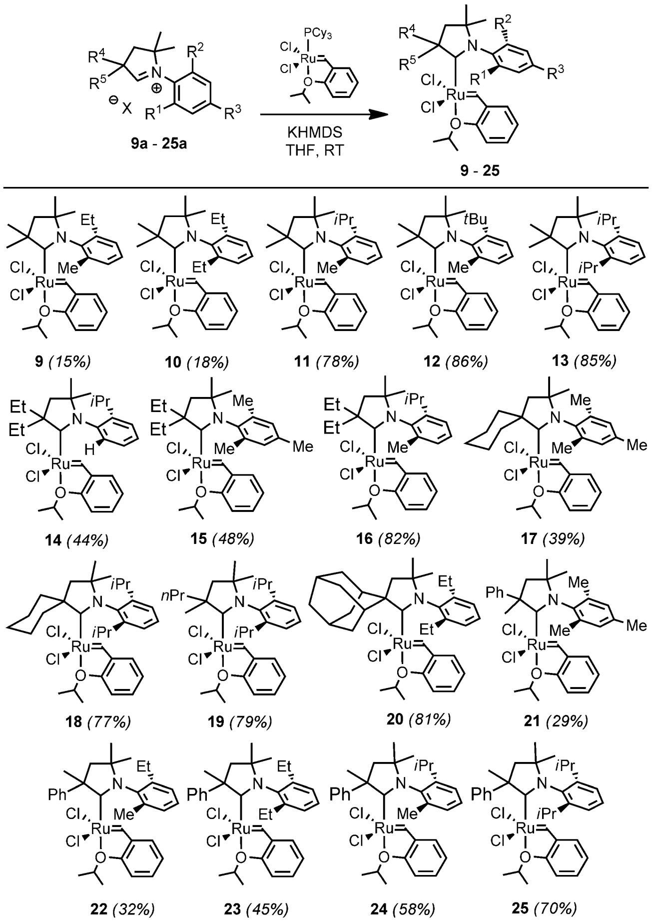
Figure 1. Selected ruthenium-based metathesis catalysts that were previously studied for ethenolysis.

high as 470 000 have been achieved with **8** in the CM of MO and 2-butene.[7] The most active catalyst for ethenolysis that has been reported to date is cyclic alkyl amino carbene (CAAC) complex **10** (see Scheme 2), which has previously shown a TON of 35 000 in the CM of MO with ethylene.[4,5] As a result of the lack of a catalyst that is sufficiently active to produce terminal olefins using ethylene gas, industrial-scale ethenolysis is currently accomplished using higher olefins as ethylene surrogates.[6b] Catalyst **7**, for example, is able to achieve the in situ ethenolysis of MO with a TON as high as 192 900 with propylene gas.[4a] However, there is a need to develop catalysts capable of achieving high activity in ethenolysis reactions when ethylene gas is utilized directly. While CM with higher olefins necessarily results in the production of a substantial amount of undesired internal olefins as by-products, the only products derived from CM with ethylene are terminal olefins. This intrinsic advantage promotes both increased yield and ease of purification of the desired terminal-olefin products, and is a particularly important consideration for biorefinery feedstocks, from which multiple downstream products are produced.[3]

Herein, we report the discovery of the most active ethenolysis catalysts to date. In many cases, TONs surpassing 100 000 were achieved for the ethenolysis of MO using ethylene gas. Remarkably, certain catalyst systems even exhibited TONs approaching 200 000, with the highest TON achieved being 330 000. For the first time, reaction conditions have been developed in order for ethenolysis to proceed efficiently on an industrial scale.

Despite the promising results previously achieved with catalyst **10** in the ethenolysis of MO,[4,5] CAAC-ligated ruthenium complexes have yet to be investigated in detail. In particular, we envisioned that more in-depth structure–activity relationship (SAR) studies would facilitate the development of new, more efficient catalysts. Thus, a variety of new catalysts were prepared through modifications of existing procedures (Scheme 2).[5,8] Known CAAC catalysts (**10**, **13**, **18**, **25**) were screened alongside the new catalysts in order to ensure accurate SAR comparisons within the series.

Initially, derivatives of the previous benchmark catalyst **10** were prepared, in which only the substituents in the *ortho* position of the N-aryl rings were varied (**9**–**13**). It is worthy to note that the syntheses of **9** and **10** are low yielding (ca. 20 %) and that their purification is cumbersome. Furthermore, complexes that bear even smaller *ortho* substituents, such as N-mesityl or N-2-isopropylphenyl, could not be accessed in even small amounts. In contrast, **11**–**13** were produced in high yields (78–86 %) and isolated without difficulty. We hypothesized that this result is related to the stability of the free carbene intermediate that is generated in situ, which might otherwise decompose rapidly in the absence of steric protection. We envisioned the circumvention of this decomposition pathway through the installment of larger substituents at either R^4 or R^5. Indeed, this strategy proved to be successful, and we were able to readily access a variety of new complexes in moderate to high yields (29–82 %). Several of the catalysts containing this more sterically hindered backbone included N-aryl substitution that was previously inaccessible (**14**, **15**, **17**, **21**), meanwhile others (**16**, **18**–**20**, **22**–**25**) were synthesized in order to provide a more thorough SAR study. Single-crystal X-ray diffraction of **11** and **24** showed distorted square-pyramidal geometries, and the structural parameters, including bond lengths and angles, were consistent with those found previously for **10** and **13** (Figure 2). Moreover, catalyst **24** bears a CAAC ligand that features a chirogenic center as well as two different substituents in the *ortho* position of the N-aryl ring. Accordingly, the single-crystal structure of **24** showed both N-aryl rotamers (**24a** and **24b**) in a ratio of 64:36.[9]



9 *(15%)* **10** *(18%)* **11** *(78%)* **12** *(86%)* **13** *(85%)*

14 *(44%)* **15** *(48%)* **16** *(82%)* **17** *(39%)*

18 *(77%)* **19** *(79%)* **20** *(81%)* **21** *(29%)*

22 *(32%)* **23** *(45%)* **24** *(58%)* **25** *(70%)*

Scheme 2. Synthesis of the CAAC complexes under study (yields of isolated complexes in brackets).

Once in hand, catalysts **9**–**25** were examined in the ethenolysis of **1** using ethylene (Table 1). Reaction conditions were adapted from those that were reported previously, and were initially re-optimized using benchmark catalyst **10** (neat MO, 40 °C, 150 psi ethylene).[4] The only deviation from the published procedures was the use of ethylene of a higher

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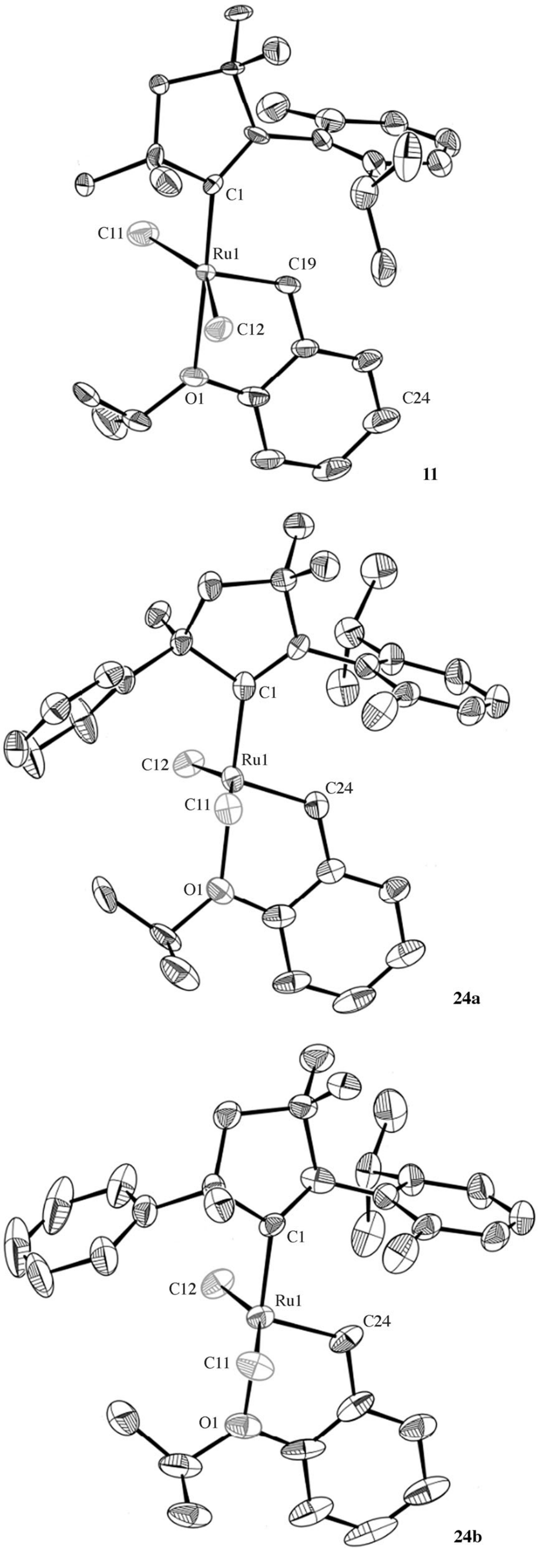

Figure 2. Solid-state structures of **11** and **24** (**24** crystallized as **24a** and **24b**, in a ratio of 64:36), with thermal ellipsoids drawn at 50% probability.[14] For clarity, hydrogen atoms have been omitted. Selected bond lengths [Å] for **11**: C1–Ru 1.928(6), C19–Ru 1.824(6), O1–Ru 2.301(4), Cl1–Ru 2.3374(16), Cl2–Ru 2.3165(17); for **24a**: C1–Ru 1.940(7), C24–Ru 1.836(9), O1–Ru 2.332(8), Cl1–Ru 2.3356(18), Cl2–Ru 2.3271(13); for **24b**: C1–Ru 1.931(12), C24–Ru 1.828(18), O1–Ru 2.325(15), Cl1–Ru 2.335(4), Cl2-Ru 2.307(3).

Table 1: Ethenolysis of methyl oleate (**1**) using catalysts **9–25**.[a]

Catalyst	Conversion [%][b,c]	Selectivity [%][b,d,e]	Yield [%][f]	TON[g]
9	37	86	32	110000
10	42	88	37	120000
11	59	92	54	180000
12	18	94	17	57000
13	19	97	18	60000
14	22	63	14	47000
15	26	86	22	73000
16	42	92	39	130000
17	19	78	14	47000
18	13	97	13	43000
19	16	97	15	50000
20	< 5%	–	–	–
21	41	83	34	110000
22	46	85	39	130000
23	48	88	43	140000
24	57	94	54	180000
25	47	98	46	150000

[a] Reaction conditions: catalyst (3 ppm), C_2H_4 (150 psi, 99.95% purity), 40°C, 3 h. [b] Determined by GC using dodecane as an internal standard. [c] Conversion = 100−[(final moles of **1**)×100/[initial moles of **1**]. [d] Selectivity for ethenolysis products (**3** and **4**) over self-metathesis products (**3a** and **4a**). [e] selectivity = 100×(moles of **3**+**4**)/[(moles of **3**+**4**)+(2×moles of **3a**+**4a**)]. [f] yield = conversion×selectivity/100. [g] TON = yield×(initial moles of **1**/moles of catalyst)/100.

purity (99.95%) than previously reported (99.9%). We were pleased to find that this simple modification appeared to already result in a substantial increase in activity: 10 ppm loading of catalyst **10** resulted in a TON of 67000, whereas the reported benchmark TON for **10** is 35000.[4b,10–13] The TON of catalyst **10** further increased to 120000 upon reduction of the catalyst loading to 3 ppm. Thus, all subsequent reactions were run at a catalyst loading of 3 ppm, which was also expected to provide greater differentiation in activity between promising catalysts in comparison to reactions run at 10 ppm.

Remarkably, at a catalyst loading of 3 ppm, most catalysts surpassed a TON of 100000! Specifically, catalysts **11** and **24** emerged as the most efficient ones, with TONs of 180000. Catalyst activity correlates with N-aryl substitution, with larger R^1 and R^2 substituents generally resulting in higher TONs, although this can also have a deleterious effect (as in **12** and **13**, compared to **9**–**11**). The ideal combination thus far appears to be a small R^1 and a large R^2 substituent, as in catalysts **11** and **24** (R^1 = Me, R^2 = *i*Pr). Interestingly, substitution of R^5 by a phenyl ring resulted in an overall improvement of activity, especially for N-2,6-diisopropylphenyl catalyst **25**. Replacement of R^4 and/or R^5 by an ethyl, propyl, or cyclohexyl moiety did not result in a significant change in the TON (as in **15**–**19**), although an adamantyl substituent (**20**) resulted in the complete loss of activity. Interestingly, while consumption of MO appears to be the most important factor that determines the overall yield of ethenolysis products, increased N-aryl substitution on the catalyst appears to strongly favor selectivity for terminal olefins. These trends in selectivity and TON are most evident in the series of catalysts that bear a phenyl ring on the backbone at R^5 (**21**–**25**).

A plausible explanation for the high activity exhibited by CAAC catalysts in ethenolysis transformations might be the increased stabilization of the ruthenium methylidene intermediate that is generated in the presence of ethylene gas. Ruthenium methylidenes are known to decompose rapidly through the insertion of the N-aryl substituent into the methylidene carbene, which subsequently generates various ruthenium hydrides that are inactive in metathesis transformations.[15] CAAC ligands are known to be more electron donating than their N-heterocyclic carbene (NHC) counterparts.[16] Thus, when used in place of NHCs, it is expected that the increased electron density at ruthenium might somewhat stabilize the otherwise highly reactive and electron-deficient methylidene intermediate.[15b,c,17] Substitution of the substituents in the *ortho* position of the N-aryl ring with a larger sterically encumbered group would also be expected to significantly decrease the rate of termination by insertion into the $[Ru]{=}CH_2$ bond. However, increased substitution can also hinder the coordination of olefins to the ruthenium metal center. Diminished reactivity with catalysts bearing more sterically encumbered N-aryl substituents was indeed noted when initiation rates of selected catalysts (**9**–**14**) were measured following the exposure to *n*-butylvinylether.[18] When initiation rates are compared to TONs, it is clear that both the slowest initiating catalysts (**12** and **13**) and the fastest initiating catalyst (**14**) exhibit the lowest TONs (Figure 3). This is likely a result of a diminished catalytic rate for the former group and an increased susceptibility to decomposition for the latter. This study illustrates the importance of this delicate balance, as reflected in the superior TONs exhibited by catalysts **11** and **24**, which possess asymmetric N-aryl substituents. In these systems, the smaller substituent (R^1 = Me) in the *ortho* position of the N-aryl ring facilitates the rapid coordination of the incoming olefin substrate, whereas the larger substituent (R^2 = *i*Pr) prevents the decomposition of the methylidene intermediate. This asymmetry might be expected to exhibit a greater effect in CAAC-ligated catalysts, as the steric interaction of the substituents in the *ortho* position of the N-aryl ring with the two adjacent geminal methyl substituents would be expected to influence the conformation of the N-aryl ring. If the larger substituent resides closer to the ruthenium metal center, the methyl group, which is inherently more susceptible to CH insertion, would be directed away from the reactive ruthenium methylidene.

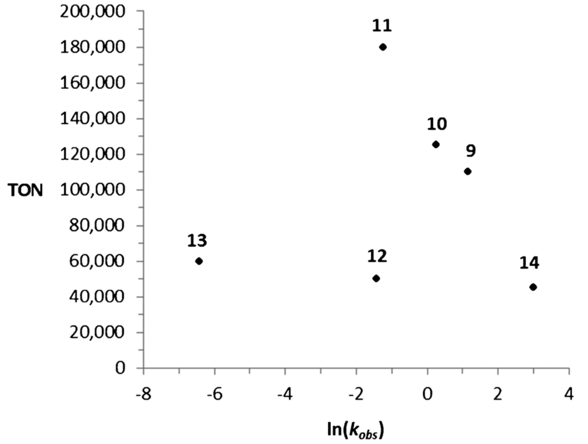

Figure 3. Comparison of initiation rates and TONs for catalysts **9**–**14**.

It has been postulated that high activity in ethenolysis might be correlated to the tendency of a catalyst to undergo degenerative metathesis events through the preferential formation of 2,4-metallacycles rather then 2,3-metallacycles, which would result in an increased selectivity for terminal olefins in the product distribution.[19] This is a powerful design principle in the context of achieving high kinetic selectivity for terminal olefins when employing higher olefins such as propene and 1-butene gas as ethylene surrogates. However, when ethylene gas is employed, it is more likely that the lower selectivities for terminal olefins exhibited by previous generations of catalysts (**5**–**8**) is primarily a result of rapid catalyst death in the presence of ethylene. This would translate to products reflecting the kinetic distribution of rapid unselective cross-metathesis reactions of **5**–**8** with both ethylene and terminal olefins.[20] Although CAAC-ligated ruthenium-based catalysts have been demonstrated to engage in metathesis reactions more slowly than phosphine- or NHC-ligated catalysts,[5a,18] they also appear to persist for a much longer time in the presence of ethylene.[21] This allows the ethenolysis reaction to proceed closer to completion in order to achieve the equilibrium ratio of terminal-olefin products, and provides a feasible explanation for the notable increase in activity exhibited by this family of catalysts.[22]

Finally, given the notable dependence of the TON on the purity of the ethylene employed, as seen earlier for catalyst **10**, we briefly explored the effect of utilizing an ethylene source with an even higher purity (99.995% vs. 99.95%) at different loadings of catalyst **11** (Table 2).[23] A dramatic increase in the TON was noted at a catalyst loading of 1 ppm. To the best of our knowledge, this represents the highest reported value for any ethenolysis catalyst to date (TON 340000).

In summary, a new series of ruthenium-based metathesis catalysts bearing CAAC ligands displays exceptional activity in ethenolysis reactions. In the cross-metathesis reaction of the seed-oil derivative methyl oleate (**1**) and ethylene gas (**2**), TONs of higher than 100000 are generated in many cases, which surpasses the minimum value of 50000 required to be considered economically sustainable on an industrial scale. Furthermore, even higher TONs (180000–340000) were obtained in some cases. These are the highest values reported to date for an ethenolysis reaction, and the only reported TONs of higher than 50000 using ethylene gas specifically. Thus, we envision that these results will find substantial

Table 2: Effect of the purity of C_2H_4 (**2**) on the activity of catalyst **11**.[a]

Loading [ppm]	Purity of **2** [%][b]	Yield [%][a]	TON[a]
3	99.95	54	180000
3	99.995	53	180000
2	99.95	48	240000
2	99.995	49	245000
1	99.95	13	130000
1	99.995	34	340000

[a] Reaction conditions and calculations as listed in Table 1.

application in the continued development of new methodologies and processes directed toward the economically and environmentally sustainable production of LAOs, as well as other valuable terminal olefins, especially through the transformation of seed oils and their derivatives.

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[9] We also observed multiple conformational and rotational isomers in the NMR spectra of each of the catalysts **21**–**24**. Ratios varied with respect to N-aryl substitution (see the Supporting Information for details).

[10] Intuitively, this marked effect might be expected. Ethylene gas contains small amounts of impurities, such as carbon monoxide and acetylene, known catalyst poisons for ruthenium-based metathesis catalysts (see Ref. [11]). At such low catalyst loadings, even trace amounts of these substances would exhibit a great effect.

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[12] Methyl oleate (Nu-Check-Prep, > 99 %) was purified through filtration over alumina (Supporting Information). As disclosed previously, this purification step is essential for high TONs (see Ref. [4]). For example, when methyl oleate purchased from Nu-Check-Prep (> 99 %) or Sigma Aldrich (> 99.0 %, Fluka analytical standard) was used without further purification, TONs were only 8500 and 230, respectively, for catalyst **11** (3 ppm).

[13] Interestingly, a similar increase was not noted for catalyst **5**. For example, under the optimized reaction conditions, **5** (100 ppm) generated a TON of only 4600 (compare with reported value of 5400, see Ref. [4b]).

[14] CCDC 1025991 (**11**) and 1025992 (**24**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[22] More detailed studies are currently underway and will be reported in due course.

[23] Ethylene gas was purchased and used as received from Matheson, and was either ultrahigh purity (99.95 %) or Matheson purity (99.995 %). Matheson purity ethylene (99.995 %) is certified to contain less than 4 ppm acetylene, and less than 2 ppm carbon monoxide.

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