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Superelectrophilic Fe(III)−Ion Pairs as Stronger Lewis Acid Catalysts for (*E*)-Selective Intermolecular Carbonyl−Olefin Metathesis

Haley Albright,[†] Hannah L. Vonesh,[†] and Corinna S. Schindler*

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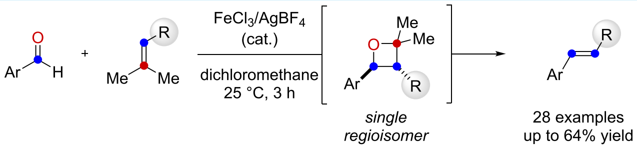
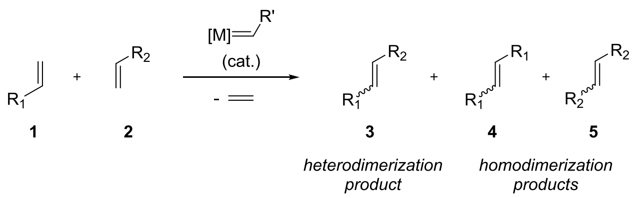
ABSTRACT: An intermolecular carbonyl−olefin metathesis reaction is described that relies on superelectrophilic Fe(III)-based ion pairs as stronger Lewis acid catalysts. This new catalytic system enables selective access to (*E*)-olefins as carbonyl−olefin metathesis products. Mechanistic investigations suggest the regioselective formation and stereospecific fragmentation of intermediate oxetanes to be the origin of this selectivity. The optimized conditions are general for a variety of aryl aldehydes and trisubstituted olefins and are demonstrated for 28 examples in up to 64% overall yield.



Olefin−olefin cross-metathesis reactions are powerful tools for direct carbon−carbon bond formation to access more complex olefins from simple olefin precursors.[1] Upon reaction with a metal alkylidene catalyst, olefins **1** and **2** are converted to the corresponding heterodimerization product **3** or homodimerization products **4** and **5** (Figure 1A).[2] The selectivity between products can be controlled depending on the choice of substrates, the relative ratio of the two olefins, and the metal alkylidene catalyst employed.[3,4] Although the formation of (*E*)-olefins as products is thermodynamically favored, a mixture of both diastereomers is often observed.[2] In recent years, carbonyl−olefin metathesis reactions have seen increased interest as a result of their ability to directly form carbon−carbon bonds between carbonyl and olefin functionalities.[5−8] Lewis-acid-catalyzed approaches have been developed as part of these efforts and undergo an initial [2 + 2]-cycloaddition to form intermediate oxetanes and a subsequent retro-[2 + 2]-cycloreversion to yield the corresponding carbonyl−olefin metathesis products.[9] On the basis of this design principle, viable procedures for carbonyl−olefin ring-closing and ring-opening metatheses, as well as transannular carbonyl−olefin metathesis, have been reported that proceed through oxetane intermediates.[10−13] Additional approaches to intermolecular carbonyl−olefin cross-metathesis exist, relying on either zeolites[14] or carbocations as organocatalysts.[12,15,16] In comparison with olefin−olefin cross-metathesis, the currently available protocols for carbonyl−olefin cross-metathesis reactions remain significantly underdeveloped. We herein report studies toward an intermolecular carbonyl−olefin cross-metathesis reaction between aromatic aldehydes **6** and olefins **7** that relies on superelectrophilic Fe(III)−ion pairs[17] as stronger Lewis acid catalysts. The reaction is found to be selective for one of three possible products via four diastereomeric oxetane intermediates (*cis*- and *trans*-**8** and -**9**) (Figure 1B).

A. Olefin-Olefin Cross-Metathesis (CM).



B. This work: (*E*)-Selective Carbonyl-Olefin Metathesis.

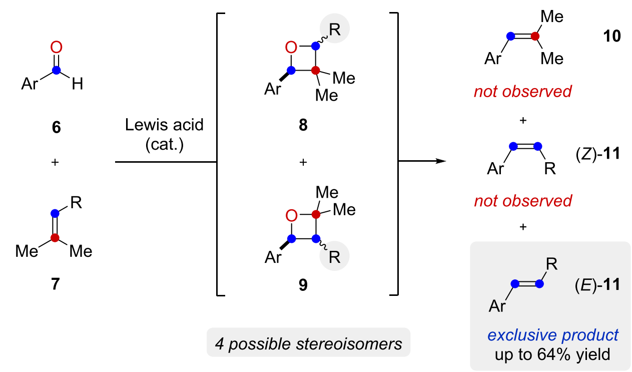


Figure 1. (A) Olefin−olefin cross-metathesis. (B) (*E*)-Selective carbonyl−olefin cross-metathesis relying on Fe(III)−ion pairs.

The mechanistic studies reported in this Letter are consistent with regiospecific oxetane formation and the

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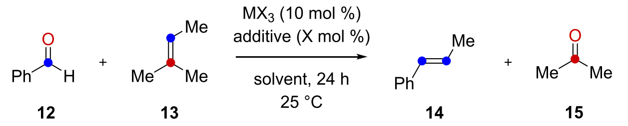
subsequent stereospecific oxetane fragmentation, which accounts for the high selectivity in products. Insights gained from this work are expected to guide future reaction development and catalyst design to expand and improve the synthetic utility of available protocols.

Table 1. Reaction Optimization for Intermolecular Carbonyl–Olefin Metathesis[a]



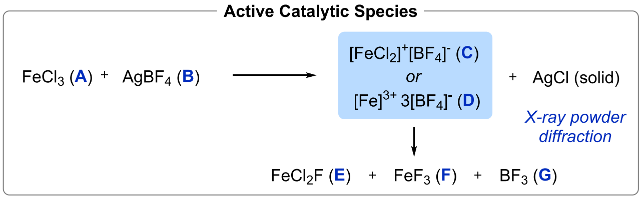
entry	Lewis acid	additive	mol %	solvent	yield **14** (%)
1[b]	$BF_3·Et_2O$	–	–	DCM	28
2[b]	$FeCl_3$	–	–	DCM	19
3[b]	$FeCl_3$	–	–	DCE	16
4[b]	$FeCl_3$	–	–	toluene	2
5[b]	$GeCl_3$	–	–	DCM	17
6[b]	$AlCl_3$	–	–	DCM	0
7[b]	$Fe(OTf)_3$	–	–	DCM	30
8[b]	$Sc(OTf)_3$	–	–	DCM	26
9[c]	$FeCl_3$	$AgOT_S$	30	DCM	0
10[c]	$FeCl_3$	$AgAsF_6$	30	DCM	31
11[c]	$FeCl_3$	$AgSbF_6$	30	DCM	24
12[c]	$FeCl_3$	$AgPF_6$	30	DCM	36
13[d]	**$FeCl_3$**	**$AgBF_4$**	**30**	**DCM**	**51**
14[c]	$FeCl_3$	$AgBF_4$	30	DCM	28
15[c]	$FeCl_3$	$AgBF_4$	30	DCM	27
16[c]	$FeCl_3$	$AgBF_4$	30	DCM	20
17[c]	$FeCl_3$	$AgBF_4$	30	DCM	35
18[e]	$FeCl_3$	$AgBF_4$	30	DCM	27
19[f]	$FeCl_3$	$AgBF_4$	30	DCM	19

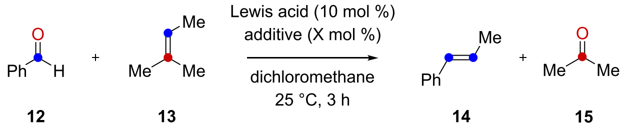
[a] Conditions: All reactions were performed using 5.0 equiv of the substrate **12** and 1 equiv of **13** in DCM (0.3 M) at 25 °C for 24 h. [b] Yields are reported based on NMR analysis. [c] Yields are reported based on GC analysis. [d] Yields are reported based on isolated yield. [e] 2.0 equiv of **12** was used. [f] 1.0 equiv of **12** was used.

The initial studies toward the development of an intermolecular carbonyl–olefin metathesis reaction focused on benzaldehyde **12** and 2-methyl-2-butene **13** as substrates (Table 1). Early efforts identified benzaldehyde **12** and 2-methyl-2-butene **13** in a 5:1 ratio as optimal for the transformation. (See the Supporting Information for additional details.) Franzén and coworkers were able to achieve 60% yield of **14** with 20 mol % of $TrBF_4$ as the cationic catalyst and otherwise identical conditions as entry 1, Table 1.[15] Catalytic amounts of $BF_3·OEt_2$ and $FeCl_3$ promoted the desired intermolecular carbonyl–olefin metathesis reaction in 28 and 19% yield, respectively (entries 1 and 2, Table 1). In comparison, decreased yields of **14** were observed with other solvents, including dichloroethane and toluene, under otherwise identical reaction conditions (entries 3 and 4, Table 1). $GaCl_3$ was analogous to $FeCl_3$ and resulted in the desired metathesis product in 17% yield (entry 5, Table 1), whereas stronger Lewis acids, such as $AlCl_3$, proved ineffective in promoting the desired carbonyl–olefin metathesis reaction (entry 6, Table 1). Promising results were also obtained with catalytic amounts of metal triflates, $Fe(OTf)_3$ and $Sc(OTf)_3$, resulting in the formation of (*E*)-olefin **14** in increased yields of 30 and 26%, respectively (entries 7 and 8, Table 1). Recently, we were able to show that heterobimetallic ion pairs,[17] resulting upon halide abstraction from neutral metal salts (MX_n) with silver salts (AgX),[18] can function as Lewis acidic superelectrophiles for catalytic carbonyl–olefin metathesis reactions. The addition of catalytic amounts of silver salts in combination with $FeCl_3$ as the Lewis acid resulted in increased yields of the desired carbonyl–olefin metathesis product **14** (entries 9–13, Table 1). Specifically, $AgBF_4$ was identified as the superior silver salt together with $FeCl_3$, providing (*E*)-olefin in 51% yield (entry 13, Table 1). Stoichiometric amounts of $AgBF_4$ under otherwise identical conditions resulted in diminished yields of **14** in 28% (entry 14, Table 1). Decreasing loadings of $AgBF_4$ of 10 and 20 mol % also proved inferior and formed **14** in 27 and 20%, respectively (entries 15 and 16, Table 1). $GaCl_3$ (which had similar yields to $FeCl_3$) was evaluated in combination with 30 mol % of $AgBF_4$; however, the transformation provided a diminished yield of 35% (entry 17, Table 1). Importantly, (*E*)-olefin **14** was observed as the exclusive carbonyl–olefin metathesis product for all Lewis acids and reaction conditions evaluated (Table 1).

Subsequent efforts focused on obtaining experimental support for heterobimetallic ion pairs as the active catalytic species under the optimal reaction conditions. Several distinct Lewis acidic species could be operative as the active catalyst: $FeCl_3$ (**A**), $AgBF_4$(**B**), heterobimetallic ion pairs $[FeCl_2]^+[BF_4]^-$ (**C**), and $[Fe]^{3+}3[BF_4]^-$ (**D**), resulting from chloride abstraction, or $FeCl_2F$ (**E**), FeF_3 (**F**), and BF_3 (**G**), formed via fluoride transfer or the decomposition of **C** and **D** (Table 2). As previously demonstrated, substoichiometric amounts of $FeCl_3$ formed metathesis product **14** in 19% yield, whereas the sole use of $AgBF_4$ failed to promote the desired carbonyl–olefin metathesis reaction (entries 1 and 2, Table 2). Equimolar loadings of 10 mol % $FeCl_3$ and $AgBF_4$ were also able to catalyze the reaction, although in a low yield of 20%

Table 2. Determination of Active Catalytic Species[a]





entry	species	Lewis acid	additive	*X* mol %	yield **14** (%)
1[b]	A	$FeCl_3$	–	–	19
2[c]	B	–	$AgBF_4$	30	0
3[d,e]	C	$FeCl_3$	$AgBF_4$	10	20
4[c,e]	**D**	**$FeCl_3$**	**$AgBF_4$**	**30**	**51**
5[c]	E	$FeCl_3$	AgF	10	4
6[c]	F	$FeCl_3$	AgF	30	9
7[b]	F	FeF_3	–	–	0
8[b]	G	$BF_3·Et_2O$	–	–	28

[a] Conditions: All reactions were performed using 5.0 equiv of the substrate **12** and 1.0 equiv of **13** in DCM (0.3 M) at 25 °C for 3 h. [b] Yields were determined via NMR with $PhMe_3Si$ as an internal standard. [c] Yields were based on isolated yield. [d] Yields were reported based on GC analysis. [e] Formation of AgCl was observed.

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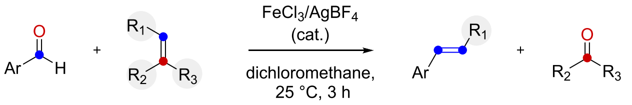
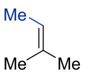
Table 3. Olefin Evaluation for Intermolecular Carbonyl−Olefin Metathesis[d]

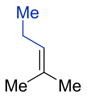


6 **16** **17** **18**

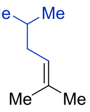
Olefin scope



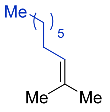
13[a] 51%[c]



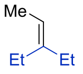
19[a] 26%[c]



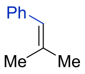
20[b] 40%[c]



21[b] 31%[c]



22[b] 23%[c]



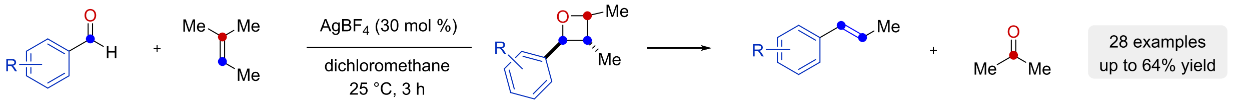
23[a] 0%[c]

[a]With benzaldehyde as aldehyde. [b]With 4-chlorobenzaldehyde as aldehyde. [c]Yields denote the metathesis product formation of each olefin substrate displayed above. [d]Conditions: All reactions were performed with 5.0 equiv of **6** and 1.0 equiv of olefin substrates **16** with 10 mol % $FeCl_3$ and 30 mol % $AgBF_4$ in DCM (0.3 M) at 25 °C for 3 h.

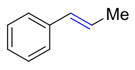
(entry 3, Table 2). In comparison, the optimal reaction conditions relying on $FeCl_3$ (10 mol %) and $AgBF_4$ (30 mol %) provided the desired product **14** in 51% yield (entry 4, Table 2). The quantitative formation of AgCl, as a white solid, was observed over the course of this transformation.[19] Utilizing $FeCl_3$ (10 mol %) and AgF (10 mol %) also resulted in the formation of product, suggesting that $FeCl_2F$ may be formed under these conditions, albeit **14** was observed in only 4% yield (entry 5, Table 2). Similarly, 30 mol % AgF together with substoichiometric amounts of $FeCl_3$ resulted in only 9% yield of the desired metathesis product (entry 6, Table 2). Additionally, FeF_3 was not an active catalyst for this transformation, confirming that it does not form in the presence of F^- ions from the $AgBF_4$ additive. Furthermore, when the reaction was conducted with $BF_3 \cdot Et_2O$ (10 mol %), the desired metathesis product **14** was observed in a diminished yield of 28% (entry 8, Table 2). Collectively, these results suggest the formation of $[FeCl_2]^+[BF_4]^-$ and $[Fe]^{3+}3[BF_4]^-$ as heterobimetallic ion pairs that serve as the active catalytic species under optimal conditions for the intermolecular carbonyl−olefin metathesis.

The olefin substrate scope for intermolecular carbonyl−olefin cross-metathesis reactions relying on superelectrophilic Fe(III)−ion pairs was next investigated (Table 3). Specifically, the substitution of longer aliphatic chains on the olefin substrate, including ethyl, isobutyl, and *n*-heptyl, was found to be compatible with the optimal reaction conditions and formed the respective metathesis products in up to 40% yield (**19**−**21**, Table 3). 2-Ethyl-2-pentene, **22**, was also found to be reactive and provided a 23% yield of the corresponding metathesis product, whereas styrene derivative **23** proved unreactive for metathesis. Importantly, the corresponding (*E*)-olefins were the exclusive metathesis products observed over the course of these transformations. Following the investigation into the olefin substrates, the aldehyde substrates were evaluated upon their ability to undergo the desired intermolecular carbonyl−olefin metathesis reaction (Table 4). para-Substituted aryl aldehydes with both electron-withdrawing and electron-donating groups proved viable under the reaction conditions, resulting in up to a 62% yield of the metathesis products (**24**−**33**, Table 4). Polyaromatic substrates including phenanthrene- and fluorene-derived aryl aldehydes effectively promoted the metathesis in low to moderate yields of 27 and 51%, respectively (**34** and **35**, Table 4). ortho-, meta-, para-, and multi-substituted aldehydes were compatible with the optimized conditions for intermolecular carbonyl−olefin metathesis and formed the desired products in yields of up to 64% (**36**−**41**, Table 4). Additionally, 2-

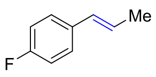
Table 4. Evaluation of the Aldehyde Substrate Scope for Intermolecular Carbonyl−Olefin Metathesis Relying on Fe(III)−Ion Pairs[a]



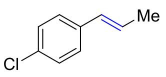
Substrate Scope



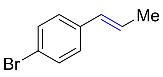
14 (51%)



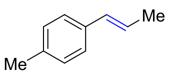
24 (47%)



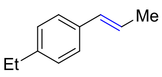
25 (56%)



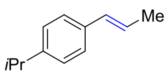
26 (51%)



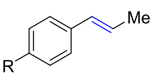
27 (56%)



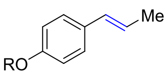
28 (47%)



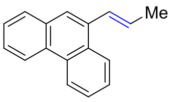
29 (60%)



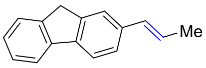
30 (R = *t*Bu, 62%)
31 (R = Ph, 56%)



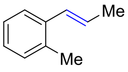
32 (R = Me, 60%)
33 (R = Bn, 25%)



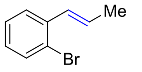
34 (27%)



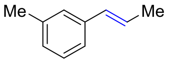
35 (51%)



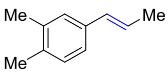
36 (60%)



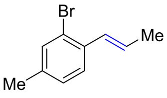
37 (18%)



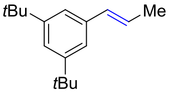
38 (58%)



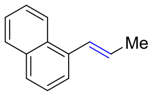
39 (53%)



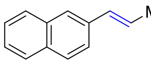
40 (59%)



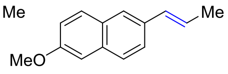
41 (64%)



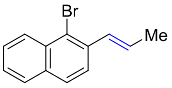
42 (0%)



43 (43%)



44 (35%)



45 (43%)

[a]Conditions: All reactions were performed with 5.0 equiv of aldehyde and 1.0 equiv of olefin substrates $FeCl_3$ (30 mol %) and $AgBF_4$ (30 mol %) in dichloromethane (0.3 M) at 25 °C for 3 h.

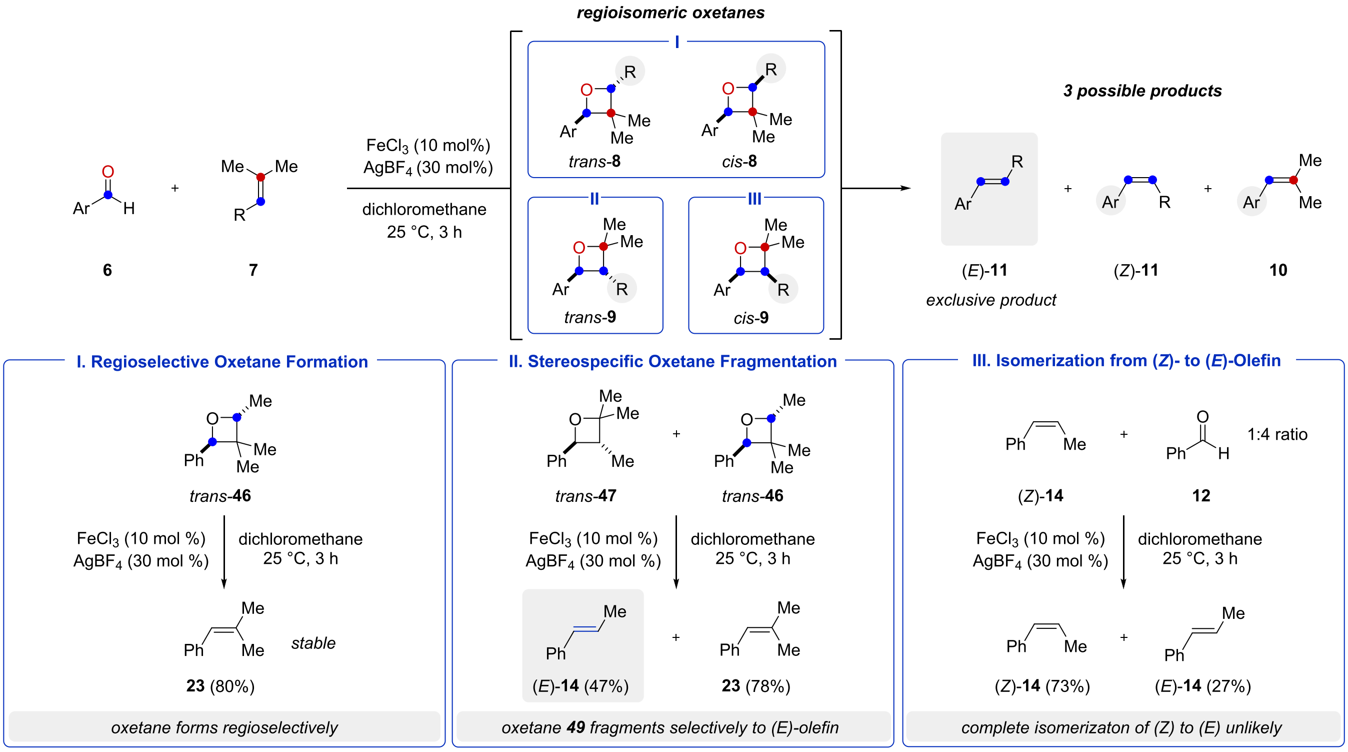


Figure 2. Experiments in support of regioselective oxetane formation and stereospecific oxetane fragmentation under the optimal reaction conditions for intermolecular carbonyl−olefin metathesis.

naphthaldehyde substrates provided moderate yields of up to 43% (**43**−**45**, Table 4). In accordance with the previous observations made during the initial reaction optimization and the investigation of the olefin substrate scope, the corresponding (*E*)-olefins were the only observed products for this transformation.

The next efforts aimed to determine the origin of the high (*E*)-selectivity observed in this transformation. Upon the addition of aryl aldehydes **6** and olefins **7**, four distinct oxetane stereoisomers could form (Figure 2). *cis*- and *trans*-oxetanes **9** would be expected as the major isomers as a result of the carbonyl oxygen atom adding to the more electrophilic carbon of the olefin, and *cis*- and *trans*-oxetanes **8** are predicted to be the minor products formed. The fragmentation of these oxetane intermediates could result in three distinct metathesis products: (*E*)-**11** formed upon the fragmentation of *trans*-**9**, (*Z*)-**11** resulting from *cis*-**9**, and trisubstituted alkene **10** as the product obtained from both *cis*- and *trans*-**8**. *trans*-**46**[20] was synthesized independently via the Paternò−Büchi reaction and subjected to the optimal conditions to gain insight into whether oxetane formation proceeds regioselectively (Figure 2I). The sole product formed was trisubstituted olefin **23**, which proved stable under reaction conditions. This olefin is not observed under the optimal conditions for intermolecular carbonyl−olefin metathesis, which suggests that regioisomeric oxetanes *cis*- and *trans*-**8** are not formed as reactive intermediates in this reaction, confirming the lack of observed olefin product **10**. To probe whether the fragmentation of oxetane *trans*-**9** proceeds stereospecifically (Figure 2II), oxetane *trans*-**47**[20] was accessed via Paternò−Büchi reaction protocols as a mixture of isomers (Figure 2II). *trans*-**47**, together with oxetane *trans*-**46**, was characterized as a mixture in a 1:2.6 ratio and subjected to the optimal reaction conditions (Figures 2II and 3). As expected, metathesis product **23** was observed in 78% yield together with (*E*)-olefin **14** in 47% yield, resulting upon the fragmentation of *trans*-**46** and *trans*-**47**, respectively. Importantly, the corresponding stereoisomer (*Z*)-**11** was not observed in this transformation. On the basis of these results, the isomerization of (*Z*)-**11** could also rapidly proceed under the optimized reaction conditions. To test this hypothesis, the isomerization of (*Z*)-**14** and benzaldehyde (**12**) in a 1:4 ratio, respectively, was monitored (Figure 2III). Isomerization from (*Z*)-**14** to (*E*)-**14** was observed, however, in only 23% yield over the

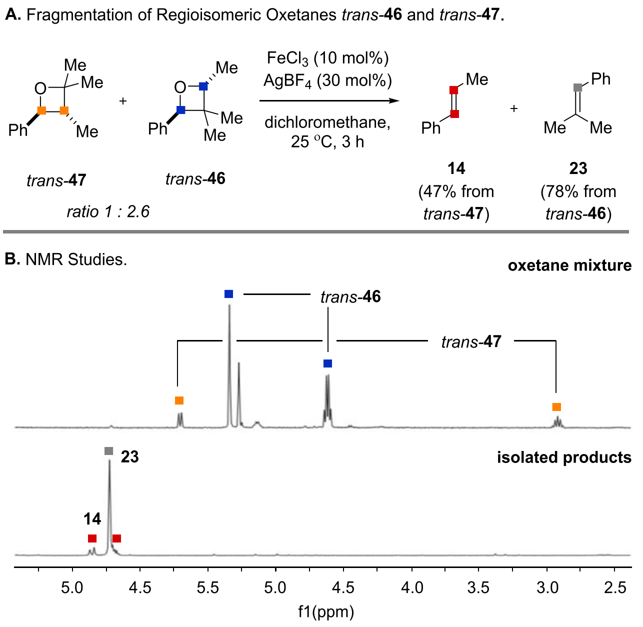


Figure 3. NMR fragmentation study of oxetane stereoisomers.

course of the reaction. Together, these results suggest the regioselective formation and the subsequent stereospecific fragmentation of an oxetane intermediate to result in the exclusive formation of (*E*)-olefin products.

The intermolecular carbonyl–olefin metathesis reaction of benzaldehyde (**6**) and trisubstituted olefin **23** was monitored via ^{1}H NMR. (See the Supporting Information for details.) The formation of the (*E*)-olefin metathesis product is evident within the first 5 min and becomes the major product in the solution after 3 h. Additionally, studies have been performed to determine if competing carbonyl-ene reaction pathways are responsible for the diminished overall yield observed in intermolecular carbonyl–olefin metathesis reactions.[21] However, no byproducts resulting via carbonyl-ene intermediates could be isolated, which is in stark contrast with the previously developed $GaCl_3$-catalyzed carbonyl–olefin ring-opening metathesis reactions developed in our group. Consequently, the diminished yields are hypothesized to be the result of competing decomposition pathways during either oxetane formation or fragmentation (Figures 2II and 3).

The studies of Lewis-acid-catalyzed intermolecular carbonyl–olefin metathesis reactions have revealed significant insights into the reaction pathway. Specifically, the metathesis reaction proceeds via a distinct regioisomer of the four possible oxetane intermediates to result in the selective formation of the (*E*)-olefin metathesis product. The lower yields observed in this method are determined to be due to competing decomposition pathways during oxetane formation and the subsequent fragmentation. The insights presented herein are expected to enable the development of more efficient catalyst systems to promote this transformation and to develop this reaction design into a platform of general synthetic utility.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00917.

Experimental procedures and HRMS and NMR studies (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Corinna S. Schindler – *Department of Chemistry, Willard Henry Dow Laboratory, University of Michigan, Ann Arbor, Michigan 48109, United States*; orcid.org/0000-0003-4968-8013; Email: corinnas@umich.edu

Authors

Haley Albright – *Department of Chemistry, Willard Henry Dow Laboratory, University of Michigan, Ann Arbor, Michigan 48109, United States*

Hannah L. Vonesh – *Department of Chemistry, Willard Henry Dow Laboratory, University of Michigan, Ann Arbor, Michigan 48109, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c00917

Author Contributions

[†]H.A. and H.L.V. contributed equally.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Handbook of Metathesis*, 2nd ed.; Grubbs, R. H., Wenzel, A. G., O'Leary, D. J., Khosravi, E., Eds.; Wiley-VCH: Weinheim, Germany, 2015; Vols. *1*–*3*.

(2) Grela, K. *Olefin Metathesis: Theory and Practice*; Wiley-VCH: Weinheim, Germany, 2014.

(3) Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. New Approaches to Olefin Cross-Metathesis. *J. Am. Chem. Soc.* **2000**, *122*, 58–71.

(4) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. A General Model for Selectivity in Olefin Cross Metathesis. *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370.

(5) For carbonyl–olefin metathesis reactions proceeding via oxetane photoadducts, see: (a) Jones, G., II; Schwartz, S. B.; Marton, M. T. 374 Regiospecific Thermal Cleavage of Some Oxetan Photoadducts: Carbonyl-Olefin Metathesis in Sequential Photochemical and Thermal Steps. *J. Chem. Soc., Chem. Commun.* **1973**, *11*, 374–375. (b) Jones, G., II; Acquadro, M. A.; Carmody, M. A. Long-chain Enals *via* Carbonyl-Olefin Metathesis. An Application in Pheromone Synthesis. *J. Chem. Soc., Chem. Commun.* **1975**, 206–207. (c) Carless, H. A. J.; Trivedi, H. S. New Ring Expansion Reaction of 2-t-Butyloxetans. *J. Chem. Soc., Chem. Commun.* **1979**, *8*, 382–383. (d) D'Auria, M.; Racioppi, R.; Viggiani, L. Paternò-Büchi Reaction Between Furan and Heterocyclic Aldehydes: Oxetane Formation vs. Metathesis. *Photochem. Photobiol. Sci.* **2010**, *9*, 1134–1138. (e) Pérez-Ruiz, R.; Gil, S.; Miranda, M. A. Stereodifferentiation in the Photochemical Cycloreversion of Diastereomeric Methoxynaphthalene-Oxetane Dyads. *J. Org. Chem.* **2005**, *70*, 1376–1381. (f) Pérez-Ruiz, R.; Miranda, M. A.; Alle, R.; Meerholz, K.; Griesbeck, A. G. An Efficient Carbonyl-Alkene Metathesis of Bicyclic Oxetanes: Photoinduced Electron Transfer Reduction of the Paternò-Büchi Adducts from 2,3-Dihydrofuran and Aromatic Aldehydes. *Photochem. Photobiol. Sci.* **2006**, *5*, 51–55. (g) Valiulin, R. A.; Kutateladze, A. G. Harvesting the Strain Installed by a Paternò-Büchi Step in a Synthetically Useful Way: High-Yielding Photoprotolytic Oxametathesis in Polycyclic Systems. *Org. Lett.* **2009**, *11*, 3886–3889. (h) Valiulin, R. A.; Arisco, T. M.; Kutateladze, A. G. Double-Tandem $[4\pi+2\pi]\cdot[2\pi+2\pi]\cdot[4\pi+2\pi]\cdot[2\pi+2\pi]$ Synthetic Sequence with Photoprotolytic Oxametathesis and Photoepoxidation in the Chromone Series. *J. Org. Chem.* **2011**, *76*, 1319–1332. (i) Valiulin, R. A.; Arisco, T. M.; Kutateladze, A. G. Photoinduced Intramolecular Cyclopentanation vs Photoprotolytic Oxametathesis in Polycyclic Alkenes Outfitted with Conformationally Constrained Aroylmethyl Chromophores. *J. Org. Chem.* **2013**, *78*, 2012–2025.

(6) Fu, G. C.; Grubbs, R. H. Synthesis of Cycloalkenes *via* Alkylidene-Mediated Olefin Metathesis and Carbonyl Olefination. *J. Am. Chem. Soc.* **1993**, *115*, 3800–3801.

(7) For Brønsted and Lewis-acid-mediated carbonyl–olefin metathesis reactions, see: (a) Schopov, I.; Jossifov, C. A Carbonyl-Olefin Exchange Reaction — New Route to Polyconjugated polymers, 1. A New Synthesis of Polyphenylacetylene. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 659–662. (b) Soicke, A.; Slavov, N.; Neudörfl, J.-M.; Schmalz, H.-G. Metal-Free Intramolecular Carbonyl-Olefin Metathesis of *ortho*-Prenylaryl Ketones. *Synlett* **2011**, *2011*, 2487–2490. (c) Knölker, H.-J.; Baum, G.; Graf, R. Lewis Acid Promoted [2 + 2] Cycloaddition of Allylsilanes and Unsaturated Esters: A Novel Method for Cyclobutane Construction. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1612–1615. (d) Jossifov, C.; Kalinova, R.; Demonceau, A. Carbonyl Olefin Metathesis. *Chim. Oggi* **2009**, *40*, 85–87.

(8) For organocatalytic approaches, see: (a) Griffith, A. K.; Vanos, C. M.; Lambert, T. H. Organocatalytic Carbonyl-Olefin Metathesis. *J.*

Am. Chem. Soc. **2012**, *134*, 18581−18584. (b) Hong, X.; Liang, Y.; Griffith, A. K.; Lambert, T. H.; Houk, K. N. Distortion-Accelerated Cycloadditions and Strain-Release-Promoted Cycloreversions in the Organocatalytic Carbonyl-Olefin Metathesis. *Chem. Sci.* **2014**, *5*, 471−475. (c) Zhang, Y.; Jermaks, J.; MacMillan, S. N.; Lambert, T. H. Synthesis of 2H Chromenes via Hydrazine-Catalyzed Ring-Closing Carbonyl-Olefin Metathesis. *ACS Catal.* **2019**, *9*, 9259−9264. (d) Jermaks, J.; Quach, P. K.; Seibel, Z. M.; Pomarole, J.; Lambert, T. Ring-Opening Carbonyl-Olefin Metathesis of Norbornenes. *ChemRxiv* **2019**, DOI: 10.26434/chemrxiv.11385774.v1. (e) Lambert, T. H. Development of a Hydrazine-Catalyzed Carbonyl-Olefin Metathesis Reaction. *Synlett* **2019**, *30*, 1954−1965.

(9) For a review on Lewis-acid-catalyzed carbonyl−olefin metathesis reactions, see: Ludwig, J. R.; Schindler, C. S. Lewis Acid Catalyzed Carbonyl-Olefin Metathesis. *Synlett* **2017**, *28*, 1501−1509.

(10) (a) Ludwig, J. R.; Zimmerman, P. M.; Gianino, J. B.; Schindler, C. S. Iron(III)-Catalysed Carbonyl-Olefin Metathesis. *Nature* **2016**, *533*, 374−379. (b) McAtee, C. M.; Riehl, P. S.; Schindler, C. S. Polycyclic Aromatic Hydrocarbons *via* Iron(III)-Catalyzed Carbonyl-Olefin Metathesis. *J. Am. Chem. Soc.* **2017**, *139*, 2960−2963. (c) Ludwig, J. R.; Phan, S.; McAtee, C. M.; Zimmerman, P. M.; Devery, J. J., III; Schindler, C. S. Mechanistic Investigations of the Iron(III)-Catalyzed Carbonyl-Olefin Metathesis Reaction. *J. Am. Chem. Soc.* **2017**, *139*, 10832−10842. (d) Groso, E. J.; Golonka, A. N.; Harding, R. A.; Alexander, B. W.; Sodano, T. M.; Schindler, C. S. 3-Aryl-2,5-Dihydropyrroles *via* Catalytic Carbonyl-Olefin Metathesis. *ACS Catal.* **2018**, *8*, 2006−2011. (e) Albright, H.; Vonesh, H. L.; Becker, M. R.; Alexander, B. W.; Ludwig, J. L.; Wiscons, R. A.; Schindler, C. S. GaCl$_3$-Catalyzed Ring-Opening Carbonyl-Olefin Metathesis. *Org. Lett.* **2018**, *20*, 4954−4958. (f) Albright, H.; Riehl, P. S.; McAtee, C. C.; Reid, J. P.; Ludwig, J. R.; Karp, L. A.; Zimmerman, P. M.; Sigman, M. S.; Schindler, C. S. Catalytic Carbonyl-Olefin Metathesis of Aliphatic Ketones: Iron(III) Homo-Dimers as Lewis Acidic Superelectrophiles. *J. Am. Chem. Soc.* **2019**, *141*, 1690−1700. (g) Riehl, P. S.; Nasrallah, D. J.; Schindler, C. S. Catalytic Transannular Carbonyl-Olefin Metathesis Reactions. *Chem. Sci.* **2019**, *10*, 10267−10274. (h) Ma, L.; Li, W.; Xi, H.; Bai, X.; Ma, E.; Yan, X.; Li, Z. FeCl$_3$-Catalyzed Ring-Closing Carbonyl-Olefin Metathesis. *Angew. Chem., Int. Ed.* **2016**, *55*, 10410−10413. (i) Hanson, C. S.; Psaltakis, M. C.; Cortes, J. J.; Devery, J. J., III Catalyst Behavior in Metal-Catalyzed Carbonyl-Olefin Metathesis. *J. Am. Chem. Soc.* **2019**, *141*, 11870−11880. (j) Hanson, C. S.; Psaltakis, M. C.; Cortes, J. J.; Siddiqi, S. S.; Devery, J. J., III Investigation of Lewis Acid-Carbonyl Solution Interactions via Infrared-Monitored Titration. *J. Org. Chem.* **2020**, *85*, 820−832. (k) Rykaczewski, K. A.; Groso, E. J.; Vonesh, H. L.; Gaviria, M. A.; Richardson, A. D.; Zehnder, T. E.; Schindler, C. S. Tetrahydropyridines via FeCl$_3$-Catalyzed Carbonyl−Olefin Metathesis. *Org. Lett.* **2020**, DOI: 10.1021/acs.orglett.0c00918.

(11) Ni, S.; Franzén, J. Carbocation Catalysed Ring Closing Aldehyde-Olefin Metathesis. *Chem. Commun.* **2018**, *54*, 12982−12985.

(12) (a) Tran, U. P. N.; Oss, G.; Pace, D. P.; Ho, J.; Nguyen, T. V. Tropylium-Promoted Carbonyl-Olefin Metathesis Reactions. *Chem. Sci.* **2018**, *9*, 5145−5151. (b) Tran, U. P. M.; Oss, G.; Breugst, M.; Detmar, E.; Pace, D. P.; Liyanto, K.; Nguyen, T. V. Carbonyl-Olefin Metathesis Catalyzed by Molecular Iodine. *ACS Catal.* **2019**, *9*, 912−919. (c) Pitzer, L.; Sandfort, F.; Strieth-Kalthoff, F.; Glorius, F. Carbonyl-Olefin Cross-Metathesis Through a Visible-Light-Induced 1,3-Diol Formation and Fragmentation Sequence. *Angew. Chem., Int. Ed.* **2018**, *57*, 16219−16223. (d) Rivero-Crespo, M. A.; Tejeda-Serrano, M.; Perez-Sanchez, H.; Ceron-Carrasco, J. P.; Leyva-Perez, A. Intermolecular Carbonyl-Olefin Metathesis with Vinyl Ethers Catalyzed by Homogeneous and Solid Acids in Flow. *Angew. Chem., Int. Ed.* **2020**, *59*, 3846−3849.

(13) Catti, L.; Tiefenbacher, K. Brø nsted Acid-Catalyzed Carbonyl-Olefin Metathesis Inside a Self-Assembled Supramolecular Host. *Angew. Chem., Int. Ed.* **2018**, *57*, 14589−14592.

(14) Zhao, P.; Ye, L.; Sun, Z.; Lo, B. T. W.; Woodcock, H.; Huang, C.; Tang, C.; Kirkland, A. I.; Mei, D.; Edman Tsang, S. C. Entrapped Single Tungstate Site in Zeolite for Cooperative Catalysis of Olefin Metathesis with Brø nsted Acid Site. *J. Am. Chem. Soc.* **2018**, *140*, 6661−6667.

(15) Naidu, V. R.; Bah, J.; Franzén, J. Direct Organocatalytic Oxo-Metathesis, a *trans*-Selective Carbocation-Catalyzed Olefination of Aldehydes. *Eur. J. Org. Chem.* **2015**, *2015*, 1834−1839.

(16) Van Schaik, H.; Vijn, R.; Bickelhaupt, F. Acid-Catalyzed Olefination of Benzaldehyde. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1611−1612.

(17) (a) Watson, R.; Davis, A. J.; Gomez-Lopez, J. L.; Nasrallah, D.; Schindler, C. Superelectrophilic Aluminum(III)-Ion Pairs Promote a Distinct Reaction Path for Carbonyl-Olefin Metathesis of Medium Sized Rings. *ChemRxiv* **2019**, DOI: 10.26434/chemrxiv.9911783.v1. (b) Djurovic, A.; Vayer, M.; Li, Z.; Guillot, R.; Baltaze, J.-P.; Gandon, V.; Bour, C. Synthesis of Medium-Sized Carbocycles by Gallium-Catalyzed Tandem Carbonyl-Olefin Metathesis/Transfer Hydrogenation. *Org. Lett.* **2019**, *21*, 8132−8137.

(18) (a) Olah, G. A. Superelectrophiles. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767−788. (b) Olah, G. A.; Klumpp, D. A. *Superelectrophiles and Their Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2007.

(19) See the Supporting Information for more information on quantitative silver salt formation (Table S4).

(20) Carless, H. A. J.; Maitra, A. K.; Trivedi, H. S. Photochemical Cycloaddition of Aldehydes to Styrenes. *J. Chem. Soc., Chem. Commun.* **1979**, *0*, 984−985.

(21) See the Supporting Information for experimental procedures of carbonyl-ene reaction pathway investigations.