

Chemical Science

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: U. P. N. Tran, G. Oss, D. P. Pace, J. Ho and T. V. Nguyen, *Chem. Sci.*, 2018, DOI: 10.1039/C8SC00907D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Chemical Science

EDGE ARTICLE

Tropylium-Promoted Carbonyl-Olefin Metathesis Reactions

Uyen P. N. Tran,^a Giulia Oss,^a Domenic P. Pace,^a Junming Ho^{*a} and Thanh V. Nguyen^{*a}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

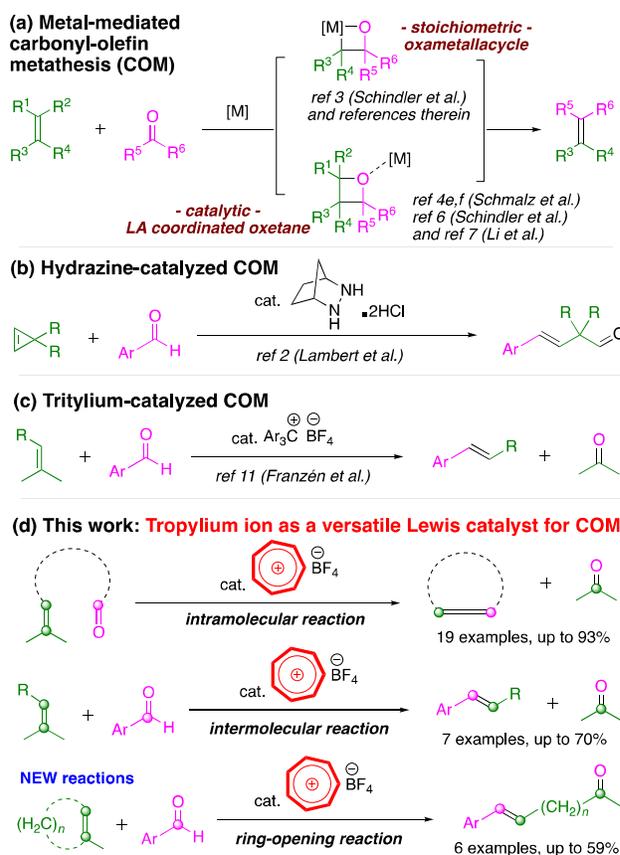
www.rsc.org/

The carbonyl-olefin metathesis (COM) reaction is a highly valuable chemical transformation in a broad range of applications. However, its scope is much less explored compared to analogous olefin-olefin metathesis reaction. Herein we demonstrate the use of tropylium ion as a new effective organic Lewis acid catalyst for both intramolecular and intermolecular COM and new ring-opening metathesis reactions. This represents a significant improvement in substrate scope from recently reported developments in this field.

Introduction

The olefin-olefin metathesis reaction has been extensively studied in the past decades due to its applicability in direct carbon-carbon bond formation.¹ The analogous carbonyl-olefin metathesis (COM) reaction,² however, is much less investigated, despite the fact that chemistry of carbonyl compounds has been exploited ubiquitously in organic synthesis.³ There might be several reasons for this, with one linked to the same versatile reactivity of the carbonyl functionality such that other chemical transformations often compete and overshadow the possible metathesis reaction.²⁻³ Until recently, there were only a small number of stoichiometric Lewis acid-facilitated protocols⁴ for the COM reaction (Scheme 1a) and relevant stoichiometric olefination reactions of carbonyl moieties.⁵

In the last two years, the Schindler's group⁶ and Li's group⁷ reported elegant studies in which they utilized salts of iron(III), an abundant transition metal,⁸ to promote intramolecular cyclization COM reactions (Scheme 1a). However, the full potential of this chemical transformation^{3,9} has not been adequately studied for ring-opening¹⁰ (Scheme 1b) or intermolecular^{2,11} (Scheme 1c) COM reactions, which are typical variations of the well-studied olefin-olefin metathesis. Therefore, the substrate scope of the COM reaction needs to be expanded beyond intramolecular cyclization to deliver the prospective synthetic applications it invokes.^{3,9} Although iron(III) catalysts have enjoyed some success, the infancy status of this field beckons further exploratory work in developing a more diverse catalyst pool for the COM reaction. Based on our previous work on the aromatic tropylium ion,¹² we envisage that tropylium could be a suitable organocatalyst



Scheme 1. Carbonyl-Olefin Metathesis (COM) Reactions

for the carbonyl-olefin metathesis reaction. The concept of using an organic compound as promoter for this type of reaction became attractive after recent developments from the Lambert's group using hydrazine² and Franzen's group using tritylium salts.¹¹ The former system catalyzed the reaction via the formation of covalently bonded hydrazonium intermediate¹³ while the latter catalyst activated the carbonyl

^a School of Chemistry, University of New South Wales, Australia
E-mail: t.v.nguyen@unsw.edu.au and junming.ho@unsw.edu.au.

† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data and NMR spectra and Gaussian coordinates. See DOI: 10.1039/x0xx00000x



compound *via* Lewis acid-base coordination. The electrophilicity of the unsubstituted tropylium ion, as reported by Mayr and co-workers, is comparable to that of tritylium ions stabilized by electron-donating substituents such as methoxy group.¹⁴ Tropylium ion¹⁵ might therefore be a suitable Lewis acid catalyst with adequate electrophilicity and oxophilicity for the COM reaction.^{12e} Gratifyingly, our study demonstrated that tropylium ion could indeed be used as an organic Lewis acid catalyst to efficiently promote the carbonyl-olefin metathesis reaction with good to excellent outcomes on a broad range of substrates. This organocatalytic system is of particular interest for future developments in this field as it proves to be a universally versatile promoter for both inter- and intra-molecular reactions as well as the new *ring-opening carbonyl-olefin metathesis*.

Results and Discussions

Intramolecular COM Reactions with Tropylium Catalyst

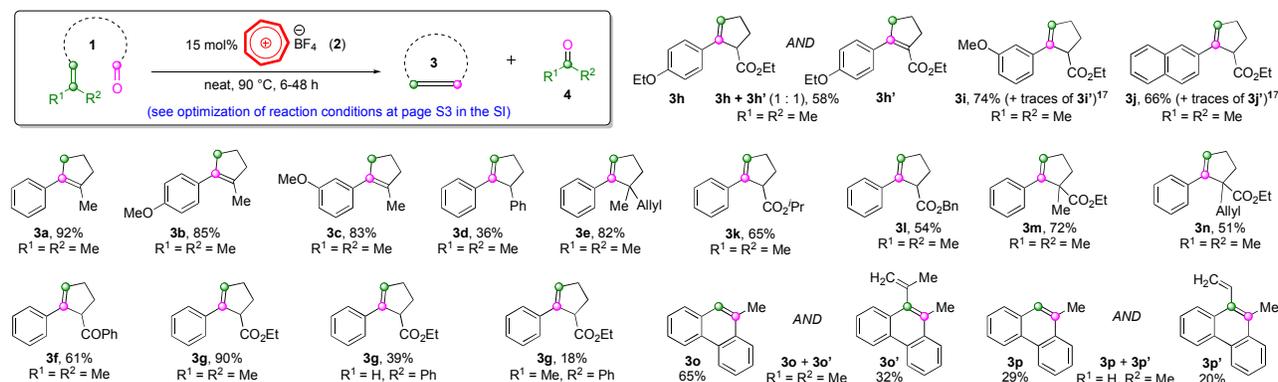
Our proof-of-concept study met with instant success for the cyclization COM reaction of substrate **1a** (Scheme 2, also see Table S1 in page S3 in the Supporting Information – SI for optimization of reaction conditions), a substrate known to work smoothly from Schindler's work employing iron(III) catalyst.^{6a} The *non-paramagnetic* nature of the tropylium organocatalyst enabled us to follow the progress of this reaction by NMR spectroscopy as illustrated in Figure 1 (also see Figure S1 in the SI for more details). The conversion of a similar substrate (**1b**, also see Scheme 2) to **3b** and acetone (**4a**, $(\text{CH}_3)_2\text{C}=\text{O}$ at 2.2 ppm) over time was very clean and completed after *ca.* 48 h at 45 °C. Similar to Schindler's iron(III) catalytic reaction, **3b** was formed as the thermodynamically favored olefin product.^{6a} We subsequently applied the intramolecular COM reaction to a broad range of substrates (Scheme 2).¹⁶ Most of tested precursors went through the tropylium-catalyzed COM reactions smoothly to afford the cyclized products in moderate to excellent yields.

Notably, substrates with methyl substituents at the α -position to the original carbonyl group normally produced the rearranged thermodynamically stable olefin products (**3a–3c**, Scheme 2). On the other hand, the replacement of Me with

aryl groups or carbonyl/carboxyl moieties gave the normal ring-closing metathesis products (**3d–3n**, Scheme 2). Two biphenyl substrates gave the phenanthrene-type products (**3o** and **3p**) with significant formation of the carbonyl-ene products (**3o'** and **3p'**, Scheme 2).¹⁷ These reaction outcomes and observations are comparable to that of iron(III)-catalyzed systems reported by Schindler and co-workers,⁶ hinting that these intramolecular COM reactions probably proceeded through some analogous pathways, despite being facilitated by two totally different catalysts.

The double bond isomerization (**3a–3c**) is presumably catalyzed by trace amounts of Brønsted acid that might form if moisture was present in the reaction mixture. However, when we carried out the reactions in very anhydrous conditions (using a glovebox), the same results were observed, implying that it might not be the case. Unfortunately, further control experiments with hindered proton scavengers (such as 2,6-dimethyl or 2,6-di(*t*-butyl) pyridines) in addition to our tropylium catalyst only led to low conversion of the starting material to the product. This was exactly the outcome for other control experiments where we used those pyridine additives with Schindler's iron (III) catalyst, which hinted that the pyridines interfered with the general COM reaction. We also found that the tropylium ion reacted directly with these pyridines to form the corresponding *N*-cycloheptatrienyl pyridinium salts,^{12g} which ruled out the validity of these Brønsted pathway control experiments at this stage.

We observed a clear pattern in the reactivity of different substrates studied in Scheme 2 that the reactions generally worked more efficiently when they produced acetone as a by-product ($\text{R}^1, \text{R}^2 = \text{Me}$). When the by-products were an aldehyde ($\text{R}^1, \text{R}^2 = \text{H}$) or aromatic ketone ($\text{R}^1, \text{R}^2 = \text{Ph}$), there were dramatic decreases in product yields (**3g**, **3p**, Scheme 2). We believe that the volatility of acetone might play a role in driving the reaction equilibrium to the productive pathway (also see entry 14, Table 1). Another possibility is that the formation of acetone is particularly thermodynamically-favored for the tropylium-catalyzed ring-closing carbonyl-olefin metathesis reactions, as such phenomenon was also observed for Schindler's and Li's systems.^{6–7}



Scheme 2. Intramolecular COM reactions



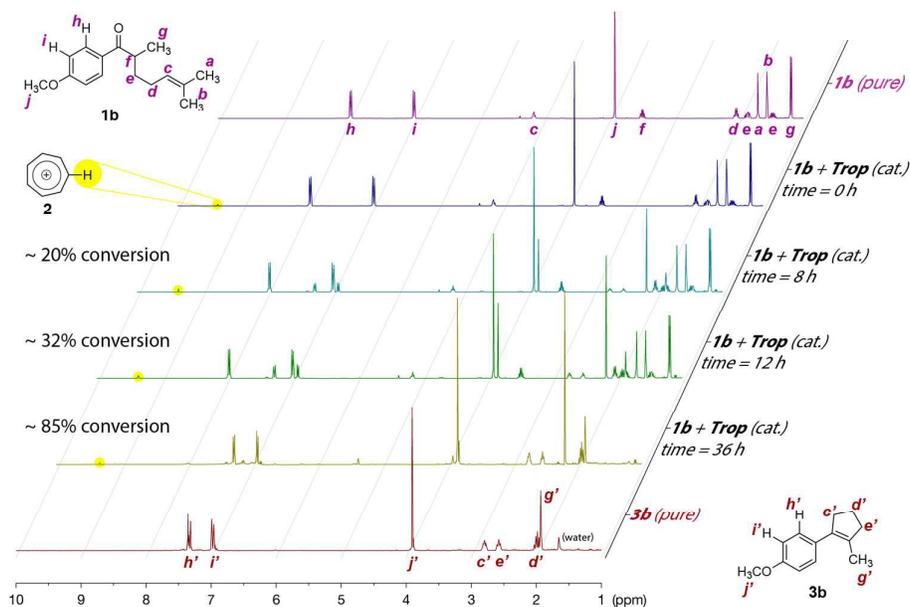


Figure 1. Progress of the tropylium-catalyzed intramolecular carbonyl-olefin metathesis reaction from **1b** to **3b** by ^1H NMR studies (CD_2Cl_2 , 25°C)

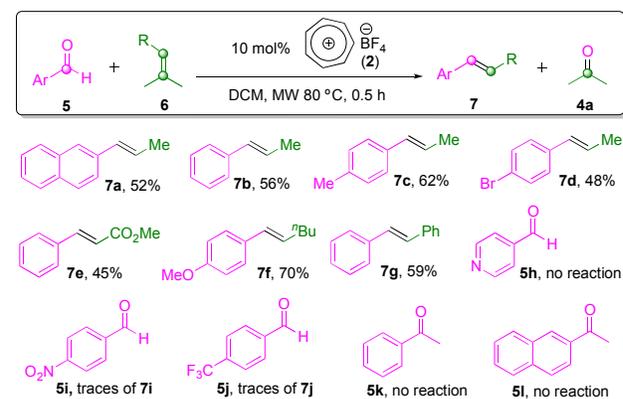
Intermolecular COM Reactions with Tropylium Catalyst

The intermolecular carbonyl-olefin metathesis is arguably a more synthetically valuable or more versatile version of this reaction (also see Scheme 1). Thus far, there has been no report on a practical catalyst system to promote this type of process,^{3,9b,9c} including Schindler's⁶ and Li's⁷ iron(III) catalysts, except the moderately successful tritylium-catalyzed reaction reported by Franzen and co-workers.¹¹ We therefore believe that it would be a challenging but suitable reaction scope to probe the catalytic activity of our tropylium catalyst. We started our investigation by looking at the intermolecular carbonyl-olefin metathesis reaction between 2-naphthaldehyde (**5a**) and alkenes (**6a**). Pleasingly, a test reaction with 20 mol% tropylium tetrafluoroborate in acetonitrile at 90°C afforded the formation of the desired product in promising yield (see page S16 in the Supporting Information for more details). Interestingly, the olefin product was formed predominantly as the *trans*-isomer,¹⁷ similar to the selectivity observed from Franzen's tritylium-catalyzed reactions.¹¹ Encouraged by this initial success, further studies were carried out on the effect of solvent, reaction temperature, catalyst loading and ratio of reagents (also see page S16 in the SI for more details). The optimal reaction conditions for the intermolecular reaction involved an excess amount of the aldehyde **5a** and 10 mol% tropylium catalyst in dichloromethane at 80°C for 0.5 hour under pressurized microwave irradiation conditions to give the COM product **7a** in 52% yield.

Thus, we subsequently applied the optimal conditions developed to a family of aromatic aldehydes and isopropylidene-bearing olefin substrates (Scheme 3). Gratifyingly, most of the electron-rich, neutral or weakly electron-poor aldehyde substrates gave the target products in moderate to good yields (**7a-7g**, Scheme 3), confirming the

feasibility and synthetic potential of the intermolecular carbonyl-olefin metathesis reactions with tropylium catalyst. In contrast to the intramolecular reaction discussed above (see Scheme 2), this intermolecular reaction however did not seem to work with ketone substrates or strongly electron-poor aromatic aldehydes. Indeed, the replacement of 2-naphthaldehyde (**5a**) with substrates such as acetophenone (**5k**) or 2-acetonaphthone (**5l**) did not produce to any observable formation of the expected metathesis products. Electron-deficient aryl aldehydes (**5j-5j**, Scheme 3) did not lead to any productive reaction outcomes either. Heteroaromatic aldehyde **5h** formed adduct with tropylium ion at the nitrogen-centre and hence deactivated the reaction system. Aliphatic aldehydes also led to complicated reaction mixtures with some aldol and carbonyl-ene¹⁸ byproducts.

The vast difference between the inter- and intramolecular reactions is presumably due to the different coordinating affinity of the weakly Lewis acidic tropylium ion to these substrate systems, but a conclusive explanation cannot be



Scheme 3. Intermolecular COM reactions.

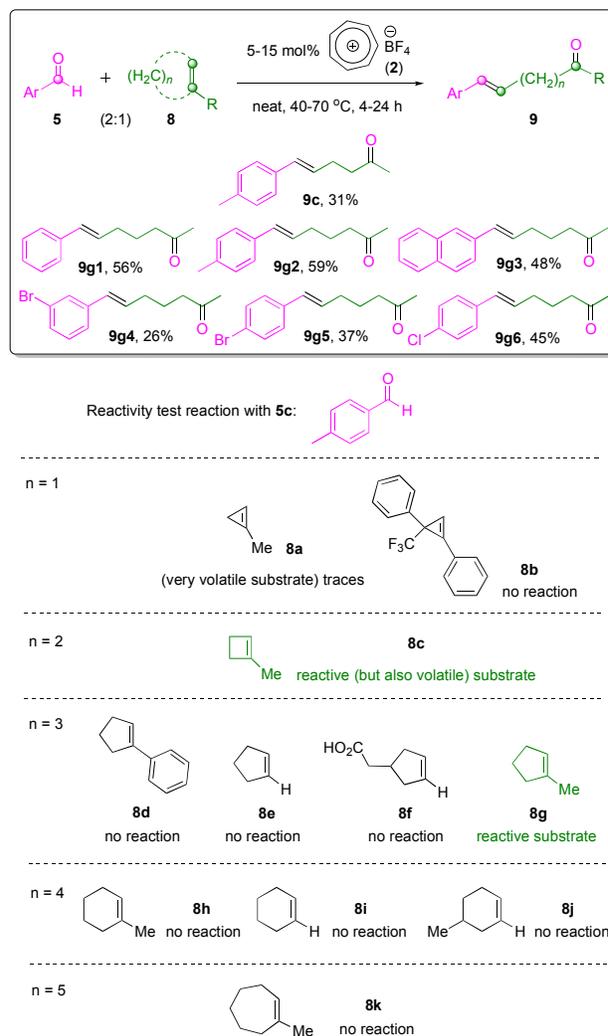


easily derived. There are also several other factors limiting the efficiency of this reaction, such as the low boiling point of alkenes and their tendency to polymerize in the presence of the tropylium catalyst. Although these intermolecular COM reactions only give moderate success, they still provide an important benchmark for this research field, as this is the only second time¹¹ the intermolecular COM reaction was investigated in catalytic sense. Both of the first study from the Franzen group with tritylium catalysts¹¹ and our study with tropylium catalyst has proven that *it might be problematic to adapt the COM reaction to bimolecular systems*. In terms of entropy change, the intermolecular COM reaction (two molecules react to form another two molecules) is presumably less favourable than the intramolecular version (one molecule cyclizes to form two products).

Intermolecular Ring-opening COM Reactions

While both catalytic intramolecular and intermolecular COM reactions have been recently realized by seminal contributions from the Schindler and Li groups⁶⁻⁷ and the Franzen group¹¹ respectively, the 'intermolecular' *ring-opening carbonyl-olefin metathesis reaction*^{10a} has been rather neglected. An elegant study from Lambert and co-workers exploited a hydrazone organocatalytic system to promote this type of reaction between aromatic aldehydes and ring-strained cyclopropene substrates.² These reactions, however, followed a totally different metathesis paradigm involving hydrazone intermediates and subsequent [2+3] cycloaddition followed by rearrangement to form the products. Therefore, it was of great interest to examine the potential of our tropylium catalyst as an organo-Lewis acid promoter for the ring-opening COM reaction in a similar manner to intra- and intermolecular reactions discussed earlier in this work.

We focus the preliminary study to the tropylium-catalyzed intermolecular ring-opening reactions (Scheme 4) of some readily accessible cycloalkenes with aromatic aldehyde **5c**, which proved to be a good substrate for the intermolecular COM reaction (Scheme 3). Interestingly, six-membered and seven-membered cycloalkenes (**8h-8k**, $n = 4$ or 5 , Scheme 4) did not metathesize to the target products while 1-methyl cyclopentene **8g** reacted smoothly to give the product **9g2** in good yield (Scheme 4). It seems that six- and seven-membered cycloalkenes probably do not possess the ring-strain necessary for the ring-opening reaction. Furthermore, a methyl substituent on the C-C double bond also helps to promote the metathesis reaction in the similar way to how acetone formation is favored for the normal intra- and inter-molecular reactions. This phenomenon is clearly demonstrated in Scheme 4 with $n = 3$, where other substituted or non-substituted cyclopentenes **8d-8f** did not react. We used this knowledge to prepare and test the ring-opening COM reaction with 1-methyl cyclobutene **8c** ($n = 2$) and 1-methyl cyclopropene **8a** ($n = 1$). These two substrates gave promising results, however the efficiency of the reactions was severely affected by their high volatility. Pressurized reaction conditions to prevent substrate evaporation led to other issues with side



Scheme 4. Intermolecular ring-opening COM reactions

oligomerization reactions, which need to be addressed by further work in reaction design. Highly-substituted cyclopropene **8b**, a substrate that we had access to from another project in our group, did not show any reactivity. We subsequently used substrate **8c** and substrate **8g** to prepare a range of ω -enone products with moderate to good yields via this newly developed ring-opening intermolecular COM reactions (Scheme 4) with aromatic aldehydes. Notably, all of the products were formed with excellent *trans*-stereoselectivity. A full investigation on the ring-opening metathesis reactions with other types of cycloalkene substrates is currently underway.

Comparison of Catalytic Activity Between Tropylium, Tritylium and Iron(III) Lewis Acid Catalysts – Role of Brønsted Acids?

As discussed above for Scheme 3, the intermolecular COM reaction seems to be the bottleneck of the development in this field. We were curious to see if iron(III) catalysts from the Schindler⁶ and Li⁷ groups, so far only known to catalyze the



intramolecular version, could address this issue. At the same time, there is also a question of whether or not Franzen's tritylium catalysts¹¹ can catalyze the ring-closing intramolecular COM reaction. To examine these questions and also to probe the efficiency of our tropylium catalytic system (**2**) to the known Schindler's iron(III)⁶ and Franzen's tritylium¹¹ catalysts, we carried out a comparative study on the intramolecular COM reaction of substrate **1g** (Scheme 5a) and the intermolecular COM reaction of substrate **5a** (Scheme 5b). Using the optimal reaction conditions developed by Schindler and Franzen for their catalytic systems^{6,11} against our catalyst, it was interesting to find out that tropylium ion can act efficiently for both intra/inter-molecular reactions while iron(III) chloride and tritylium ion seem to be good catalysts for only one type of reaction or another (Scheme 5).

It is not surprising to see the bulky tritylium ion failed to facilitate the sterically demanding intramolecular reaction; but to why the iron(III) catalyst performed poorer than expectation for the intermolecular reaction^{9b} would require further investigation. This comparison is obviously imperfect, as it does not take into account the reaction temperature and reaction time as well as catalyst loading. It is, however, indicative of the versatility of the tropylium catalyst where its electronic and steric properties in combination with oxophilicity/Lewis acidity are suitable for both inter- and intramolecular COM reactions.

As tropylium salts and many other Lewis acids (including FeCl₃) might react with moisture present in the reaction system to produce strong Brønsted acids, it is necessary to confirm that Brønsted acids, if any, are not interfering with the COM reactions. Thus, we also carried out some control studies in

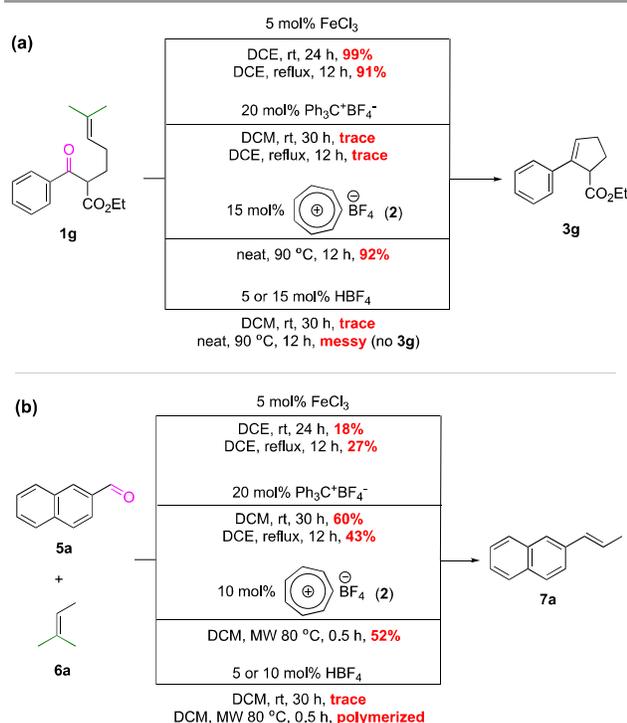
which HBF₄ was used as a potential catalyst at different loadings. These reactions were performed at various conditions for both inter- and intramolecular COM reactions (Scheme 5) but all led to non-productive outcomes. A simple Brønsted acid catalytic pathway is unlikely to be productive for the COM reaction as the Tiefenbacher has recently discovered in their interesting supramolecule-assisted COM study.¹⁹ Therefore, it can be concluded that the Lewis acidity of tropylium catalyst **2** indeed plays a crucial role in promoting the COM reactions.

Mechanistic Studies

Mechanistically, these metathesis reactions involve a non-photochemical [2+2] cycloaddition and [2+2] cycloreversion, each of which could proceed via a concerted or stepwise pathway. The former is forbidden by orbital symmetry rules, and would normally entail a barrier that is too high to overcome through thermal activation. In recent studies by Schindler and co-workers,^{6a-c} the authors demonstrated that Lewis acidic FeCl₃ could stabilize the zwitterionic intermediate (through coordination to the carbonyl oxygen) and provided compelling experimental and computational evidence to support an asynchronous concerted pathway.

To better understand the catalytic role of tropylium, we have carried out high-level *ab initio* calculations in conjunction with the SMD implicit model²⁰ to compare the energetics of three COM pathways: (1) in the absence of tropylium ion, (2) aldehyde hydrogen bonded to tropylium ion, and (3) coordination of aldehyde to tropylium ion (see page S26 in the ESI for ¹H NMR spectroscopic evidence and computational studies of tropylium-carbonyl interactions). For pathways (1) and (2), the reactants and products are connected by two concerted cycloaddition transition states and a cycloaddition intermediate (Figure 2), whilst pathway (3) involves four stepwise transition states and additionally two zwitterionic intermediates (Figure 3). Consistent with orbital symmetry rules, both pathways (1) and (2) are accompanied by very high barriers (TS₁ and TS₂) exceeding 200 kJ mol⁻¹, and are unlikely to occur under thermal activation. As shown in Figure 2, it is also interesting to note that H-bonding to tropylium ion does not provide any stabilization of the transition states. Presumably, the concerted nature of these transition states (no charged intermediates) also means that any electrostatic stabilization from tropylium is likely to be minimal.

Figure 3 shows the free energy profile for the stepwise pathway and it is evident that coordination of the anionic oxygen to tropylium ion lowers the barriers significantly. Specifically, the rate-limiting step for this pathway is about 90 kJ mol⁻¹ lower compared to the reaction in the absence of tropylium ion (153 c.f. 245 kJ mol⁻¹). This result is somewhat surprising because coordination to oxygen to form the heptatriene adduct inevitably disrupts the aromaticity of the tropylium ring. Presumably, this enthalpic cost is more than compensated when the anionic oxygen is neutralized through coordination to tropylium.



Scheme 5. Catalytic activity comparison



The structures of the stepwise transition states hint at a termolecular mechanism, although intrinsic reaction coordinate (IRC) simulations of these transition states show that they relax to reactants and products where the tropylium ion remains coordinated. On the other hand, potential energy scans indicate that addition of CO oxygen to tropylium (while the remaining atoms are constrained to positions at the transition state geometry) is approximately barrier-less (see ESI). A plausible mechanistic picture is that tropylium exists as a π -stacked complex with aldehyde **5b** (c.f. Table S3 configuration C, page S28 in the ESI), which spontaneously coordinates to the C-O oxygen as the anionic charge develops upon nucleophilic addition. Indeed, our kinetic experiments show that the rate of metathesis is first-order with respect to the concentration of tropylium ion.¹⁷ It is also worth pointing out that the computed barriers in Figure 3 are likely to represent upper bound estimates of the actual values. This is because these reactions involve the consumption of an aromatic cation (tropylium) and the generation of a localized carbocation, so the solvation contribution is likely to be under-

estimated by quantum chemical implicit solvation models.^{20b} Regardless, it is clear from the calculations that the reaction is significantly enhanced only when tropylium acts as a Lewis acid to stabilize the zwitterionic intermediate formed in the stepwise pathway.

Conclusions

We have developed a novel catalytic system employing the tropylium ion as an organo-Lewis acid to promote the carbonyl-olefin metathesis reaction. The carbonyl-olefin metathesis reaction has always been considered a highly valuable chemical transformation but much less explored than its analogous olefin-olefin metathesis. We have demonstrated that the tropylium ion can efficiently catalyze this type of reaction on a broad range of substrates, which are applicable to both intramolecular and intermolecular reactions as well as the ring-opening metathesis.

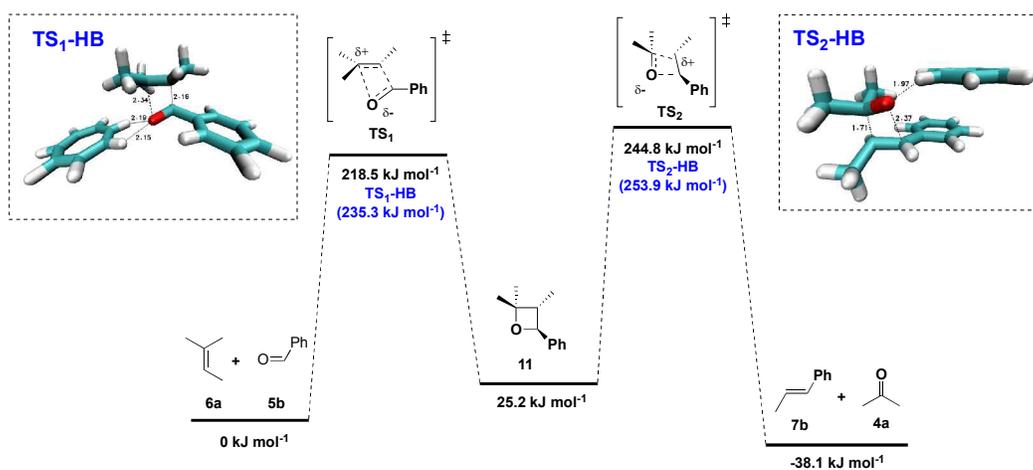


Figure 2. G3(MP2)-RAD+SMD(DCM) free energies for reactions in the absence of tropylium, and with H-bonding to tropylium. The barriers for the latter are shown in parenthesis.

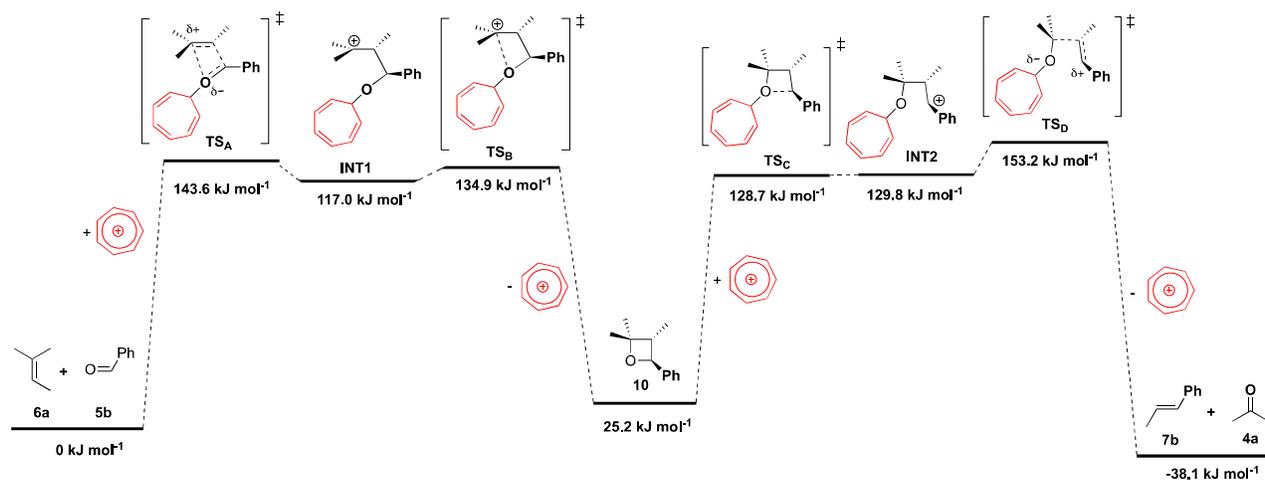


Figure 3. G3(MP2)-RAD+SMD(DCM) free energies (at 298 K) for reactions catalyzed by coordination of CO oxygen to tropylium.



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is financially supported by Australian Research Council (grant DE150100517 awarded to TVN and grant DE160100807 awarded to JH). JH acknowledges the Australian NCI and Intersect NSW for generous allocation of supercomputer resources.

Notes and references

- (a) R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413-4450; (b) A. Fürstner, *Angew. Chem. Int. Ed.*, 2000, **39**, 3012-3043; (c) Y. Chauvin, *Angew. Chem. Int. Ed.*, 2006, **45**, 3740-3747; (d) R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2006, **45**, 3760-3765; (e) R. R. Schrock, *Angew. Chem. Int. Ed.*, 2006, **45**, 3748-3759; (f) A. H. Hoveyda and A. R. Zhugralin, *Nature*, 2007, **450**, 243-251.
- A. K. Griffith, C. M. Vanos and T. H. Lambert, *J. Am. Chem. Soc.*, 2012, **134**, 18581-18584.
- J. R. Ludwig and C. S. Schindler, *Synlett*, 2017, **28**, 1501-1509.
- (a) H. A. J. Carless and H. S. Trivedi, *J. Chem. Soc., Chem. Commun.*, 1979, 382-383; (b) I. Schopov and C. Jossifov, *Makromol. Chem., Rapid Commun.*, 1983, **4**, 659-662; (c) A. C. Jackson, B. E. Goldman and B. B. Snider, *J. Org. Chem.*, 1984, **49**, 3988-3994; (d) G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, 1993, **115**, 3800-3801; (e) H.-P. van Schaik, R.-J. Vijn and F. Bickelhaupt, *Angew. Chem. Int. Ed.*, 1994, **33**, 1611-1612; (f) V. A. Khripach, V. N. Zhabinskii, A. I. Kuchto, Y. Y. Zhiburtovich, V. V. Gromak, M. B. Groen, J. van der Louw and A. de Groot, *Tetrahedron Lett.*, 2006, **47**, 6715-6718; (g) N. Slavov, J. Cvengroš, J.-M. Neudörfel and H.-G. Schmalz, *Angew. Chem. Int. Ed.*, 2010, **49**, 7588-7591; (h) A. Soicke, N. Slavov, J.-M. Neudörfel and H.-G. Schmalz, *Synlett*, 2011, **2011**, 2487-2490.
- (a) J. R. Stille and R. H. Grubbs, *J. Am. Chem. Soc.*, 1986, **108**, 855-856; (b) J. R. Stille, B. D. Santarsiero and R. H. Grubbs, *J. Org. Chem.*, 1990, **55**, 843-862; (c) K. C. Nicolaou, M. H. D. Postema and C. F. Claiborne, *J. Am. Chem. Soc.*, 1996, **118**, 1565-1566; (d) J. D. Rainier, S. P. Allwein and J. M. Cox, *J. Org. Chem.*, 2001, **66**, 1380-1386; (e) U. Majumder and J. D. Rainier, *Tetrahedron Lett.*, 2005, **46**, 7209-7211; (f) K. Iyer and J. D. Rainier, *J. Am. Chem. Soc.*, 2007, **129**, 12604-12605; (g) S. T. Heller, T. Kiho, A. R. H. Narayan and R. Sarpong, *Angew. Chem. Int. Ed.*, 2013, **52**, 11129-11133; (h) B. Hong, H. Li, J. Wu, J. Zhang and X. Lei, *Angew. Chem. Int. Ed.*, 2015, **54**, 1011-1015.
- (a) J. R. Ludwig, P. M. Zimmerman, J. B. Gianino and C. S. Schindler, *Nature*, 2016, **533**, 374-379; (b) J. R. Ludwig, S. Phan, C. C. McAtee, P. M. Zimmerman, J. J. Devery and C. S. Schindler, *J. Am. Chem. Soc.*, 2017, **139**, 10832-10842; (c) C. C. McAtee, P. S. Riehl and C. S. Schindler, *J. Am. Chem. Soc.*, 2017, **139**, 2960-2963; (d) E. J. Groso, A. N. Golonka, R. A. Harding, B. W. Alexander, T. M. Sodano and C. S. Schindler, *ACS Catal.*, 2018, 2006-2011.
- L. Ma, W. Li, H. Xi, X. Bai, E. Ma, X. Yan and Z. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 10410-10413.
- A. Fürstner, *ACS Cent. Sci.*, 2016, **2**, 778-789.
- (a) A.-L. Lee, *Angew. Chem. Int. Ed.*, 2013, **52**, 4524-4525; (b) E. T. Hennessy and E. N. Jacobsen, *Nat Chem*, 2016, **8**, 741-742; (c) C. Saá, *Angew. Chem. Int. Ed.*, 2016, **55**, 10960-10961.
- (a) G. Jones, M. A. Acquadro and M. A. Carmody, *J. Chem. Soc., Chem. Commun.*, 1975, 206-207; (b) C. Jossifov and R. Kalinova, in *Green Metathesis Chemistry*, eds. V. Dragutan, A. Demonceau, I. Dragutan and E. S. Finkelshtein, Springer Netherlands, Dordrecht, 2010, pp. 305-314.
- N. Veluru Ramesh, J. Bah and J. Franzén, *Eur. J. Org. Chem.*, 2015, 1834-1839.
- (a) T. V. Nguyen and A. Bekensir, *Org. Lett.*, 2014, **16**, 1720-1723; (b) T. V. Nguyen and M. Hall, *Tetrahedron Lett.*, 2014, **55**, 6895-6898; (c) T. V. Nguyen and D. J. M. Lyons, *Chem. Commun.*, 2015, **51**, 3131-3134; (d) D. J. M. Lyons, R. D. Crocker, M. Blümel and T. V. Nguyen, *Angew. Chem. Int. Ed.*, 2017, **56**, 1466-1484; (e) D. J. M. Lyons, R. D. Crocker, D. Enders and T. V. Nguyen, *Green Chem.*, 2017, 3993-3996; (f) G. Oss, S. D. de Vos, K. N. H. Luc, J. B. Harper and T. V. Nguyen, *J. Org. Chem.*, 2018, **83**, 1000-1010; (g) G. Oss, J. Ho and T. V. Nguyen, *Eur. J. Org. Chem.*, 2018, accepted, DOI = 10.1002/ejoc.201800579.
- X. Hong, Y. Liang, A. K. Griffith, T. H. Lambert and K. N. Houk, *Chem. Sci.*, 2014, **5**, 471-475.
- (a) H. Mayr, B. Kempf and A. R. Ofial, *Acc. Chem. Res.*, 2003, **36**, 66-77; (b) S. Minegishi and H. Mayr, *J. Am. Chem. Soc.*, 2003, **125**, 286-295; (c) M. Horn and H. Mayr, *Chem. Eur. J.*, 2010, **16**, 7478-7487; (d) M. Horn and H. Mayr, *Eur. J. Org. Chem.*, 2011, 6470-6475; (e) M. Horn and H. Mayr, *J. Phys. Org. Chem.*, 2012, **25**, 979-988; (f) M. Horn, L. H. Schappele, G. Lang-Wittkowski, H. Mayr and A. R. Ofial, *Chem. Eur. J.*, 2013, **19**, 249-263.
- (a) C. Jandl, D. C. Mayer and A. Pöthig, *Eur. J. Org. Chem.*, 2017, **2017**, 4255-4259; (b) C. Jandl and A. Pöthig, *Acta Crystallogr., Sect. C*, 2017, **73**, 810-813.
- Intramolecular reactions involved substrates with aldehyde groups gave poor conversion and complicated reaction mixtures.
- See the Supporting Information for more details.
- J. Lv, Q. Zhang, X. Zhong and S. Luo, *J. Am. Chem. Soc.*, 2015, **137**, 15576-15583.
- L. Catti and K. Tiefenbacher, *Angew. Chem. Int. Ed.*, 2018, Early View article, DOI = 10.1002/anie.201712141
- (a) J. Ho and M. Z. Ertem, M. Z. *J. Phys. Chem. B*, 2016, **120**, 1319-1329. (b) A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.



TOC entry

The non-benzenoid aromatic tropylium ion acts as an efficient promoter for carbonyl-olefin metathesis reaction.

