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Mechanistically Inspired Catalysts for Enantioselective Desymmetrizations by Olefin Metathesis

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Abstract: In asymmetric olefin metathesis reactions, the addition of halide additives is often required to augment enantioselectivities, despite the fact that the additives result in catalysts with diminished reactivities. The preparation of new chiral Ru-based catalysts was accomplished by exploiting previously reported mechanistic studies. The catalysts possess a high level of reactivity and successfully induce high levels of asymmetry in desymmetrization reactions without the use of halide additives.

Keywords: asymmetric catalysis · desymmetrization · N-heterocyclic carbenes · olefin metathesis · ruthenium

Introduction

Asymmetric olefin metathesis has tremendous potential as an asymmetric technology because it has both inter- and intramolecular variants, and results in the effective formation of carbon–carbon bonds under mild and neutral conditions.[1] Although the standard for asymmetric olefin metathesis remains the Mo-based catalysts developed by Schrock and Hoveyda, the development of chiral Ru-based catalysts such as **1** and **2** (Figure 1), has continued to gain momentum due to their bench stability and tolerance of functional groups.[2–5] In many instances, the enantioselectivity in asymmetric olefin metathesis reactions catalyzed by Ru-based catalysts is improved through the addition of NaI as an additive. This results in substitution of the Cl^- ligands bound to Ru by I^- ligands and increases the enantioselectivity of several different asymmetric processes. A downside to this strategy is that iodide substitution can also affect the reactivity of the catalyst, which is normally decreased. The lack of sufficient reactivity in a catalyst can limit its substrate scope. Herein we report the development of new highly reactive catalysts for asymmetric desymmetrization reactions that afford high enantiomeric excess (*ee*) values without the use of halide additives.

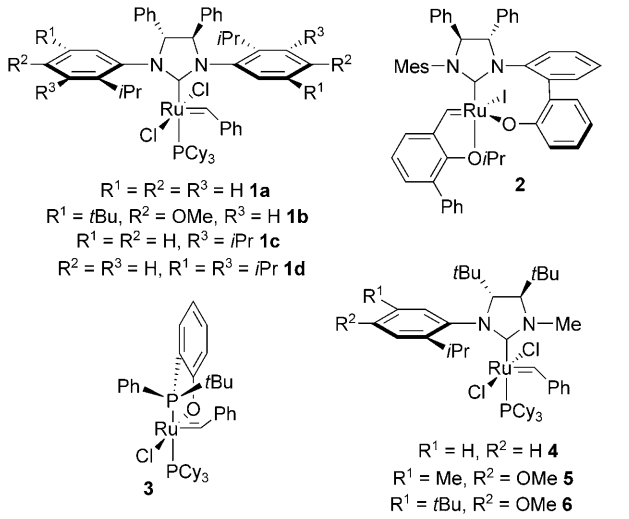

Figure 1. Olefin metathesis catalysts. PCy_3 = tricyclohexylphosphine; Mes = 2,4,6-trimethylphenyl.

Results and Discussion

Recent studies into the ligand dynamics[6] of Ru-based catalysts and the origin of stereoinduction in asymmetric Ru-catalyzed metathesis reactions[7] have shed light onto how to design more effective catalyst systems. Recently, our group

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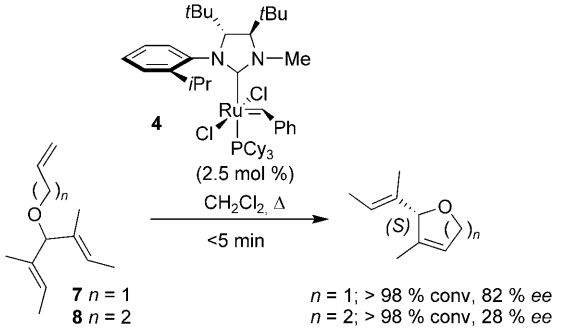
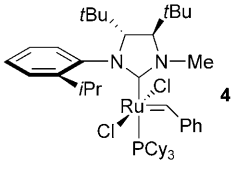
designed the new Ru-based catalyst **4**, which possesses a C_1-symmetric N-heterocyclic carbene (NHC) ligand for desymmetrization reactions.[8] The ligand design was based upon work by Chen and co-workers who prepared a Ru-based olefin metathesis catalyst **3** containing a bidentate phosphine ligand (Figure 1). During the metathesis catalytic cycle, the two different diastereomeric carbenes possible, each exhibit a different reactivity.[9] Moreover, stereoisomeric carbenes have been implicated in AROM/CM (AROM = asymmetric ring-opening metathesis, CM = cross metathesis) processes involving catalyst **2**.[10] We attempted to exploit these concepts in the design of an asymmetric catalyst. Thus, the C_1-symmetric NHC ligand of catalyst **4**,[11] was constructed with an *N*-methyl group located *syn* to the carbene to afford increased levels of reactivity. The enantioselectivity would be controlled by the *t*Bu groups of the NHC backbone, which exert a chiral relay effect upon the adjacent *N*-aryl group. Unfortunately, when catalyst **4** was used in the desymmetrization of trienes, the enantioselectivity (*ee*) varied depending on the size of the ring formed. The triene **7** underwent cyclization with **4** to afford the corresponding five-membered ring heterocycle in 82% *ee*, but the triene **8** cyclized to the corresponding six-membered ring in only 28% *ee* (Scheme 1).



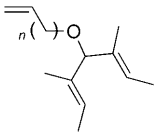
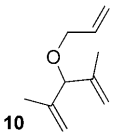
Scheme 1. Desymmetrization reactions of alkenes **7** and **8** with catalyst **4**.

Due to the abundant literature precedent indicating that iodide additives can help boost enantioselectivities in desymmetrization processes, we investigated the use of both NaBr and NaI as additives in the desymmetrization of trienes (Table 1). When the cyclization of triene **7** was conducted in the presence of NaBr, the *ee* decreased to 68% and was even lower when NaI was used (48% *ee*). *This was surprising as there were no previous reports of diminished* ee *values when halide additives were used.* In fact, Grubbs and co-workers observed a large increase in *ee* (35 to 90%) during the desymmetrization of **7**, by using NaI as an additive with catalyst **1a**. The conversion of triene **7** with either **1a** or **4** was not affected by the halide additives. Intrigued by these observations, we also conducted the same experiments with triene **8**. In the presence of NaBr or NaI additives, the *ee* values for the cyclization of **8** with catalyst **4** were observed to increase incrementally to 34 and 42% *ee* respectively. Grubbs and co-workers have reported that cyclization of **8** with catalyst **1a** in the presence of NaI affords excellent conversion (>98%) and *ee* (90%). The cyclization of triene **9** in the presence of NaBr afforded only a slight increase in *ee* to 64% from 60% and no conversion was observed when NaI was used. Triene **10** differs from **7** in that it lacks methyl groups on the olefins. The cyclization of **10** in the presence of additives afforded slight increases in *ee*. This is in contrast to what was observed with triene **7**, however the slight increase in *ee* for substrate **10** is similar to what was observed by Grubbs.

Table 1. ARCM[a] reactions with NaI and NaBr as additives.

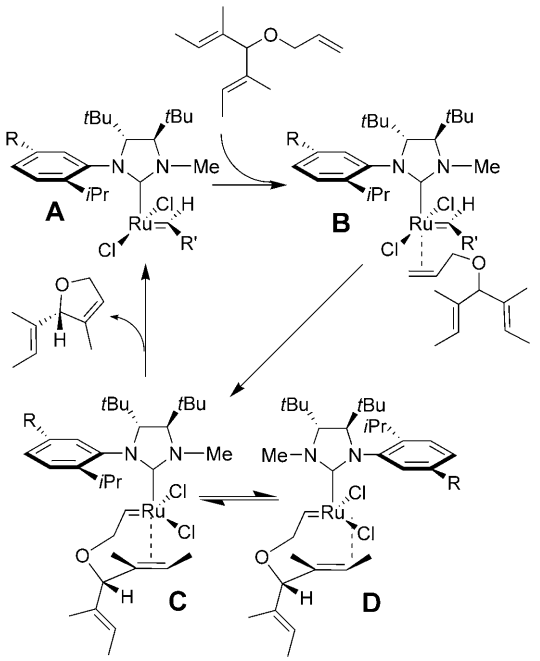


(4 mol %)
additive (1 equiv), solvent
40 °C, 2 h
triene → product
[M]= 0.055

Triene	*n*	Additive[b]	*ee* [%][c]	Conv [%][d]
	1	none	82	>98
		NaBr	68	>98
		NaI	48	>98
	2	none	28	>98
		NaBr	34	>98
		NaI	42	41
n= 1, **7**	3	none	60	>98
n= 2, **8**		NaBr	64	93
n= 3, **9**		NaI	–	–
		none	33	>98
		NaBr	35	>98
		NaI	42	>98
10				

[a] ARCM = asymmetric ring-closing metathesis. [b] The solvent was CH_2Cl_2 in the absence of additives and THF when additives were used. Catalyst **4** and the additive were stirred in THF for one hour prior to the addition of substrate. [c] Enantiomeric excesses were determined by chiral GC: see the Supporting Information for chromatograms. [d] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

The above studies demonstrate that the use of halide additives is not certain to afford high *ee* values with all substrates and catalysts. Given the failure of halide additives to induce higher levels of enantiomeric excess with catalyst **4**, we were forced to envision new catalyst modifications that could improve the enantioselection for desymmetrization of trienes such as **8** and **9**. However, any catalyst modifications would have to conserve the high reactivity observed with **4**. On examining the mechanism for olefin metathesis, we theorized that a possible explanation for the lower *ee* values observed with these trienes might be that NHC rotation is possible during the catalytic cycle (Scheme 2). The oscillation of the carbene of **4** during the catalytic cycle is depicted in Scheme 2. During the desymmetrization of trienes **7** and **8**, the ring-closing step takes place at intermediate **C**, but



Scheme 2. Catalytic cycle for olefin metathesis, which involves carbene rotation during a desymmetrization process.

the relative rate at which the ring-closing process occurs should differ because cyclization of **7** produces a five-membered ring and cyclization of **8** produces a six-membered ring. If the ring-closing reaction of **8** were to be sufficiently slow as to permit NHC rotation at intermediate **C** during the catalytic cycle, then intermediate **D** would be formed. The subsequent ring closure of intermediate **D** would take place in an achiral environment and erode the *ee*. Thus, NHC rotation may be the cause of the low *ee* values obtained in the desymmetrization to form six- and seven-membered rings,[8] in which the rate of ring closure may compete with NHC rotation.

NHC rotation has been observed in derivatives of catalyst **4**, such as when its corresponding Hoveyda version **11** was prepared. Interestingly, catalyst **11** was not formed as a single rotational isomer like **4**. In addition, NOE studies confirmed that the NHC ligand of **11** was rotating at room temperature (Figure 2).[12] If the NHC was capable of rotation in the precatalyst, it was highly likely that NHC rotation could occur during the catalytic cycle.

We were interested in seeing if NHC rotation in catalyst **11** would affect the enantioselective desymmetrizations to a significant extent compared with catalyst **4**. Interestingly, when **11** was evaluated in two desymmetrization reactions, the reactivity profile and enantioselectivities were similar to those observed with **4** (Table 2). For example, the ring closure of trienes **7** and **9** with either **4** or **11** afforded *ee* values within 1–3% of each other. Given the similarity of the results and that the NHC ligands of catalysts **4** and **11** are identical, we assume that although the NHC in **11** is rotating at room temperature, the reaction takes place in the conformation in which the *N*-methyl group is *syn* to the carbene at

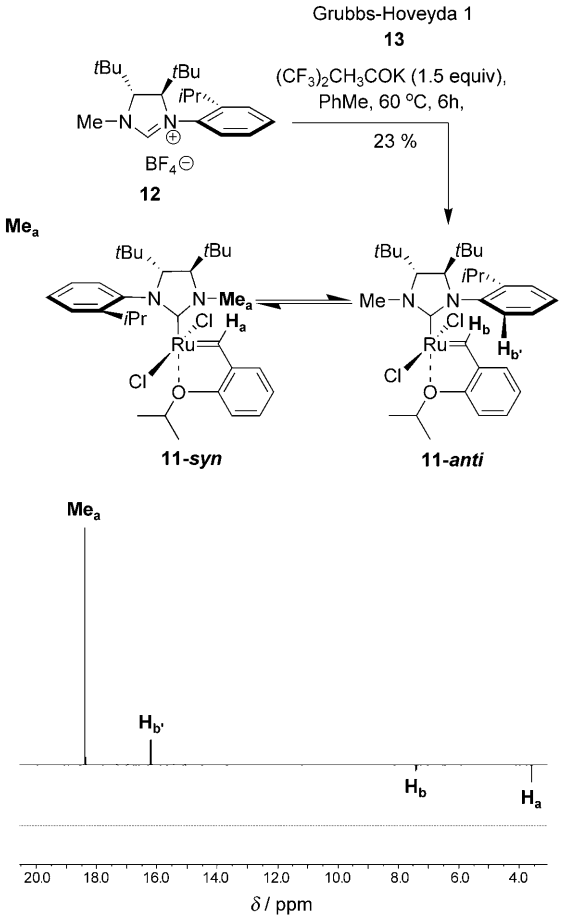
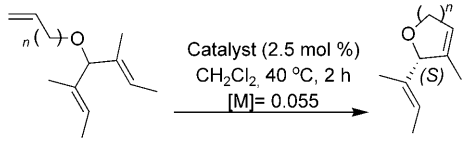


Figure 2. NOE spectroscopic analysis of catalyst **11** indicates rotation at 21 °C.

Table 2. ARCM reactions with chiral ruthenium catalysts **4** and **11**.



7 *n* = 1
9 *n* = 3

Entry	Triene	Catalyst	*ee* [%][a]	conv [%][b]
1	**7**	**4**	82	>98
		11	81	>98
2	**9**	**4**	60	>98
		11	57	>98

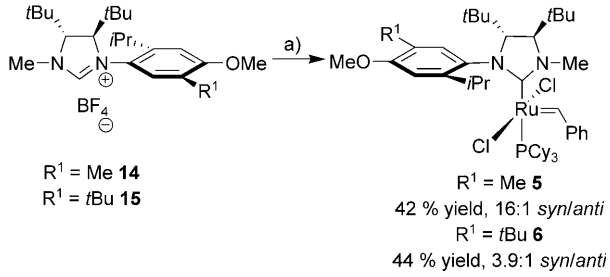
[a] Enantiomeric excesses determined by chiral GC: see the Supporting Information for chromatograms. [b] Determined by ^{1}H NMR spectrum of the crude reaction mixture.

a much faster rate than when the *N*-aryl group is *syn* to the carbene. This is purely an assumption, and it should be noted that the rates of initiation of **4** and **11** are likely to be significantly different.

Consequently, we envisioned preparing catalysts **5** and **6**, which possess additional aryl substituents (R^1, see Scheme 2). It was believed that the bulky *t*Bu or Me groups

on the *N*-aryl substituent would be oriented towards the carbene and chloride ligands and hence, might significantly hinder rotation of the NHC ligand and thus increase the energy barrier between intermediates **C** and **D** during the catalytic cycle.

The NHC ligands **14** and **15** were prepared by using established synthetic protocols[12] that were based upon those used for the preparation of catalyst **4**. The tetrafluoroborate salts **14** or **15** were treated with $(CF_3)_2CH_3COK$ and Grubbs 1st generation catalyst in toluene at 60 °C for 6 h to afford the catalysts **5** and **6** in 42 and 44 % yield respectively (Scheme 3). Both catalysts were isolated as a mixture of rotational isomers, in which NOE studies were used to deduce that there was no NHC rotation in either precatalyst at room temperature. The catalyst **5** was isolated in a 16:1 *syn*/*anti* ratio, whereas catalyst **6** was isolated in a 3.9:1 *syn*/*anti* ratio.[13] Neither of the two rotational isomers of either catalyst could be separated by column chromatography.

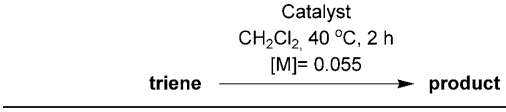


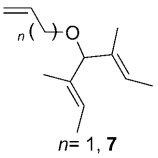
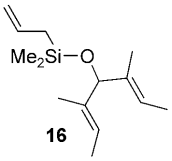
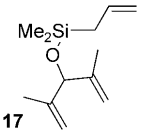
Scheme 3. Synthesis of new catalysts: reaction conditions: a) $(CF_3)_2CH_3COK$ (1.5 equiv), PhMe then $(PCy_3)_2Cl_2Ru{=}CHPh$ (1 equiv), 60 °C, 6 h. Only the major *syn* rotational isomer is shown above.

Based upon the prior observations with catalyst **4**, we assumed that metathesis reactions involving the catalysts **5** and **6** would still show a high reactivity profile similar to what was observed for catalyst **4**. Indeed, in a series of test reactions, catalysts **4** and **6** were allowed to react with triene **7** for five minutes and a >95 % conversion was observed in both cases.[14] A similar experiment was carried out with triene **16**. After five minutes, the catalyst **4** had achieved 37 % conversion to the product while catalyst **6** had already achieved 93 % conversion. Despite the fact that catalysts **5** and **6** were obtained as a mixture of isomers, their reactivity profiles are similar to or better than the parent catalyst **4**. We assume that all significant reactivity from catalysts **5** and **6** occurs from the major *syn* isomer. Hence, we would also assume that the *anti* isomers of catalysts **5** and **6** would not significantly contribute to any observed enantioselectivity obtained during desymmetrizations.[15]

We then tested catalysts **5** and **6** in various desymmetrization reactions and compared their results with those obtained with catalysts **4** and **1**(Table 3).[16,17] For all entries, catalysts **4**, **5**, and **6** are compared with catalysts containing similar *N*-aryl substituents, and with the best results obtained to date for that particular substrate.

Table 3. ARCM reactions to form five- and six-membered rings.



Triene	*n*	Catalyst[a]	Additive	*ee* [%][b]	conv [%][c]
 *n*= 1, **7** *n*= 2, **8**	1	**1b**	–	30	>98
		1b	NaI	87	>98
		1c	–	46	>98
		1c	NaI	90	>98
		4	–	82	>98
		6	–	82	>98
		5	–	81	>98
	2	**1a**	NaI	90	>98
		4	–	28	>98
		6	–	92	>98
 **16**		**1b**	–	75	>98
		1b	NaI	85	>98
		1c	–	92	>98
		1c	NaI	92	58
		4	–	6	>98
		6	–	94	>98
		5	–	75	>98
 **17**		**1a**	–	16	72
		1a	NaI	nd[d]	<2
		1d	–	45	92
		4	–	15	>98
		6	–	37	>98

[a] Catalyst loadings: **1** (2 mol %), **1** with NaI (4.0 mol %), **4**–**6** (2.5 mol %). The solvent was CH_2Cl_2 in the absence of additives and THF when additives were used. Catalysts and 25 equiv of NaI were stirred in THF for one hour prior to the addition of substrate. [b] Enantiomeric excesses were determined by chiral GC (see the Supporting Information for chromatograms). [c] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. For catalysts **4**–**6**, no other products resulting from decomposition or from homocoupling are ever observed. [d] nd = not determined.

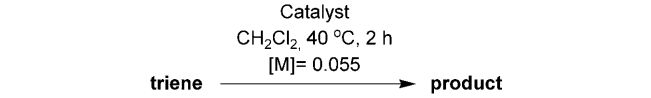
We were particularly interested in whether it was possible to consistently attain high *ee* values in the absence of additives. For the ring closure of triene **7** to afford a five-membered ring, the *ee* values obtained with catalysts **5** and **6** were similar to those obtained with catalysts **4** and **1b** when NaI was used as an additive. Catalyst **1c** can produce similarly high levels of enantiomeric excess in the desymmetrization of **7** with additives, however in the absence of NaI the *ee* decreases.

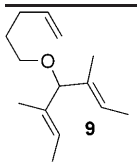
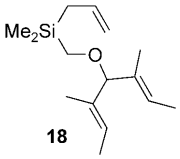
In the desymmetrization to form six-membered rings, catalyst **6** was the optimal catalyst. In the desymmetrization of **8**, the six-membered ring product was obtained in 92 % *ee*—a significant increase from the 28 % *ee* that was obtained with catalyst **4**! In addition, the *ee* is again slightly improved from that obtained with a mixture of **1a** and NaI. Similar results were obtained for the ring-closing reaction of triene **16**, which was previously isolated in very low *ee* by using catalyst **4**. Gratifyingly, the cyclization with catalysts **5** and **6** gave the product in 75 and 94 % *ee* respectively. Catalyst **1c** has been shown to afford similarly high levels of *ee* with substrate **16**, both with and without the use of NaI as an additive, however use of NaI causes the conversion to decrease

significantly. In addition, the ring closure of triene **17** with catalyst **6** also afforded a higher *ee* than was observed with **4** (37% vs. 15%). Catalyst **1a** affords the product in only 16% *ee* in the cyclization of **17** and lower conversion. Catalyst **1d** affords the highest *ee* for this substrate. In this case, the use of NaI as an additive with catalyst **1a** caused the reaction to completely shutdown, demonstrating the possible pitfalls of adding halides.

We also surveyed desymmetrizations to form seven-membered rings (Table 4). In the desymmetrization of **9** and **18**, catalyst **6** gave either comparable or slightly higher enantioselectivities than those obtained with **1c**. For example, the trienes **9** and **18** were cyclized in 88 and 94% *ee* respectively with catalyst **6**. Again, the advantage of these catalysts is that halide additives, typically added with Ru-based catalysts,[2,3,18] are not necessary to obtain high enantioselectivities. For example, the cyclization of **18** with catalyst **1a** using a NaI additive could afford similar *ee* values to catalyst **6**, but the conversion dropped to 5%. In addition, the conversions of triene **18** are higher with catalyst **6** than with **1c**.

Table 4. ARCM reactions to form seven-membered rings.



Triene	Catalyst[a]	*ee* [%][b]	conv [%][c]
	**1a**	85	5
	1c[d]	76	93
	4	60	>98
	5	71	>98
	6	88	>98
	**1c**[e]	92	65
	6	94	>98

[a] Catalyst loadings: **1** (2 mol%), **1c** with NaI (4.0 mol%), **4**–**6** (2.5 mol%). [b] Enantiomeric excesses determined by chiral GC (see the Supporting Information for chromatograms). [c] Determined by ^{1}H NMR spectrum of crude reaction mixture. For catalysts **4**–**6**, no other products resulting from decomposition or from homocoupling are ever observed. [d] The catalyst was added in two portions. [e] Only 1 mol% of catalyst was used.

Conclusion

The catalyst **6** was prepared by using mechanistic insight gained from previous studies. This catalyst affords high enantioselectivities in desymmetrization reactions without the need for halide additives. The monodentate NHC ligand of **6** was constructed by using a C_1-symmetric design to afford both high reactivity and high enantioselectivity. Catalyst **6** highlights that the rotational barrier of NHC ligands in these catalysts may play a large role in determining their reactivity and that it may be exploited in designing new asymmetric catalysts. Although many studies into improving the reactivity of Ru-based metathesis catalysts have centered on varying the structure of the benzylidene ligand,[19] there has been renewed interest in employing modified NHCs[20] to develop better catalysts, hence the studies described herein should be of interest. The results with catalyst **6** also add further weight to the molecular modelling and experimental studies, which suggest that the carbene oscillates during the catalytic cycle. The *N*-alkyl unit of the C_1-symmetric NHC is of interest. The electronic and steric effects of this unit on asymmetric olefin metathesis reactions are currently under study. We are currently evaluating catalysts analogous to **5** and **6**, which contain different *N*-alkyl groups in the hope of further clarifying the hypothesis of NHC rotation. Nonetheless, the high level of reactivity and selectivity of these catalysts could open new avenues for asymmetric olefin metathesis.

Acknowledgements

We thank the NSERC (Canada), FQRNT (Québec), CFI (Canada), Boehringer Ingelheim (Canada) Ltd., Merck Frosst Centre for Therapeutic Research and the Université de Montréal for generous financial support.

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[16] Although the high reactivity of catalyst **4** allows it to effect ring closure of five- and six-membered rings at 0 °C, the *ee* values were not significantly improved and all desymmetrizations were performed at reflux in CH_2Cl_2.

[17] The product yields from the desymmetrizations can be highly variable since many of the products are highly volatile. There is no indication that the crude reaction mixtures contain any homocoupling or decomposition products.

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