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ORIGINAL PAPER

Self and cross-metathesis of allylisothiocyanate with alkyl esters by grubbs 2nd generation catalyst

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ABSTRACT Allylisothiocyanateundergoes self-metathesis by 2nd generation Grubbs catalyst to give 1,4-disothiocyanatobut-ene together with the release of styrene and phosphine ligands. Despite the release of both ligands cross metathesis with methyl oleate, ethyl oleate and ethyl linoleatestill gave some targeted cross and self-metathesis products.1-isothiocyanatoundec-2-ene was detected in all the cross-metathesis reaction. Methyl11-isothiocyanatoundec-9-enoate and ethyl-11-isothiocyanatoundec-9-enoateare products of another cross-metathesis with methyl oleate and ethyl oleate respectively. Under the reaction conditionno other cross product with ethyl linoleate was detectedexcept the formation of side products ofcarbene species possibly due to side reactions such as isomerization and addition. The formation of 1-isothiocyanatomethylstyreneis the result of the cross metathesis between allylisothiocyanate and styrene. The study indicated that the sulfur atom is more sensitive than oxygen atom to interact with the catalyst resulting in the release of the phosphine and styrene from catalytic cycle. Therefore a suitable protecting agent is necessary to sustain the catalytic cycle.

Keywords:Allylisothiocyante, Cross metathesis, Methyl esters, Ruthenium catalyst

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INTRODUCTION

The continuing effort on the studies of metathesis of fatty acid methyl esters is driven by the formation of various important intermediates for the commercial synthesis of useful materials. Aliphatic dicarboxylic acids are known asimportant intermediates for producing biodegradable polymers(Ngo et al., 2006). Suberic (C_8), azelaic (C_9) and sebaucic acids (C_{10}) are among the intermediates those have been used for producing nylon, cosmetic, plasticizer and lubricant (Ngo et al., 2006). The study is also in line with the current trend on the use of renewable raw and low toxic materials. Earlier studies on metathesis of fatty acid methyl esters were based on vegetable oils such as soybean, sunflower,olive and linseed oilswhich are known to contain triolein(Boelhouwer&Mol, 1984; Boelhouwer&Mol, 1985).For practical and analytical conveniences the metathesis products are subjected to esterification. The products can then be analysed by gas chromatography and GCMS. The major products from theself-metathesis of fatty acid methyl ester are cyclo-hexa-1,4-diene, alkenes mono and dicarboxylic acids (Erhan, et al., 1997; Marvey, 2008). The self-metathesis of soybean oil gives branching productswith increased molecular weight. Crude palm oilwhich is one of a major world commodity of vegetable oil consists of triglycerideswith almost 50% unsaturated composition was also subjected to self-metathesis by using ChauvinWCl_6- $SnMe_4$ catalyst in dichloromethane (Nordin et al., 1991; Yarmo et al., 1992).The major products obtained were 6-pentadecene, 9-octadecene, dimethyl-9-octadecenedioate and various methyl esters.

A lot of effort and times were devoted on the catalytic development that has resulted in three Nobel laureate recipients in recognition of their contribution. Schrock and Chauvin catalysts are air sensitive and not tolerant to functionalities. However, the less air sensitive and tolerance to functionalities of ruthenium complexes pioneered by Grubbs have opened upthe scope for studying metathesisreaction with endless possibilities. The metathesisreaction in aqueous solution has also become possible(Lipshutz et al., 2008; 2011). Non-edible oil from palash tree grown in India was reported to give 9-octadecene, 9-pentadecenoic acid methylester,cyclodecylcyclotetradecene, 6-pentadecene and 3-dodecene when subjected to metathesis using 2^{nd} generation Grubbs catalyst (Vyshnavi et al., 2014).On the other hand the cross metathesis of methyl esters has received much attention recently. The cross metathesis of methyl oleatewith acrolein (Bonin et al., 2015) and methyl acroylate (Vignon et al., 2014) were found to be useful for the production of diesters. We have recently studied the cross metathesis of methyl oleate with several olefins including terminal, symmetrical and highly functionalised olefin containing oxygen and silicon atoms and found that 2^{nd} generation catalyst was quite an efficient catalyst (Awang et al., 2016). The conversion and yields of the self and crossed metathesis products could be controlled by varying the substrate to crossing agent ratios. To study the effect ofnucleophilic atom in a functional group such as thiocyanateon the tolerance of the catalyst herein we report the self and cross metathesis of allylisothiocyanate with alkyl esters.

MATERIALS AND METHODS

All experiments were carried out under a nitrogen atmosphere in a vacuum atmosphere dry box unless otherwise stated. All chemical used were reagent grades and purified by the standard purification procedure. Anhydrous grade dichloromethane (DCM) was transferred into a bottle containing molecular sieve in the dry box. Allylisothiocyanate (AT) (Sigma Aldrich), methyl oleate, MO (Fluka), ethyl oleate, EO (NacalaiTesque) and ethyl linoleate, AL(Fluka) were used in the dry box as received without purification. The catalyst tricyclohexylphosphine(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazole-2-ylidenebenzyl lidineruthenium(IV) dichloride(Aldrich Chemical Co) was used in the dry box as received.

GC-MS analysis of metathesized products

The reaction products were analysed by using an Agilent 7890A gas chromatograph (GS) directly coupled to the mass spectrometer system (MS)of the Agilent5975C inert MSD with triple-axis detector.The Agilent 7890A is equipped with BP-20 or DB-5MS UI column (30m x 0.25mm x 0.25μm) and stationary phase 5% phenylmethylpolysiloxane. Mass Spectrometer operating in the EI mode (70 eV;m/z 40-600; source temperature 230 °C and a quadrapole temperature 150 °C. The column temperature was initially maintained at 40°C for 3 minutes, increased to 220°C at 5°C/min with a hold time of 11 min at 220°C. The inlet temperature was maintained at 220°C and splitless. Helium was used as the carrier gas at the flow rate of 1.3 ml min^{-1}.Structural assignments were based on interpretation of mass spectrometric fragmentation and confirmed by comparison of retention times as well as fragmentation pattern of authentic compounds and the spectral data obtained from MSD chemstation using the NIST/EPS/NIH version 2.0.

Typical self and cross metathesis reaction

Preliminary study on the self-metathesis of allylisothiocyanate was carried out by reacting 2^{nd}generation Grubbs catalyst (4.2mg, 0.1mmol) andallylisothiocyanate (9.9mg, 0.1mmol) in 10 ml of DCM at room temperature (rt). The mixture was stirred for 24 h. The brown colour solution turned dark brown after 24 h of stirring. The reaction solution was allowed to pass through a small column containing celite before the GC-MS experiment. Similar procedure wasapplied for the cross-metathesis reaction but with an addition of crossing agent. The effect of time of reaction on the product formation was also carried out.

RESULTS AND DISCUSSION

Self metathesis of allylisothiocyanate

1,4-diisothiocyanatobut-2-ene (SM1) is the only possible product of self-metathesis of allylisothiocyanate. The brown solution of the mixture of isothiocyanate and the catalyst slowly turned dark brown after stirring. No precipitate of Ru or ruthenium oxide was observed indicating the catalytic system is functioning well. However, the gas chromatogram of the solution after 1 h reaction time shows 8 major peaks with some minor peaks(Fig. 1).

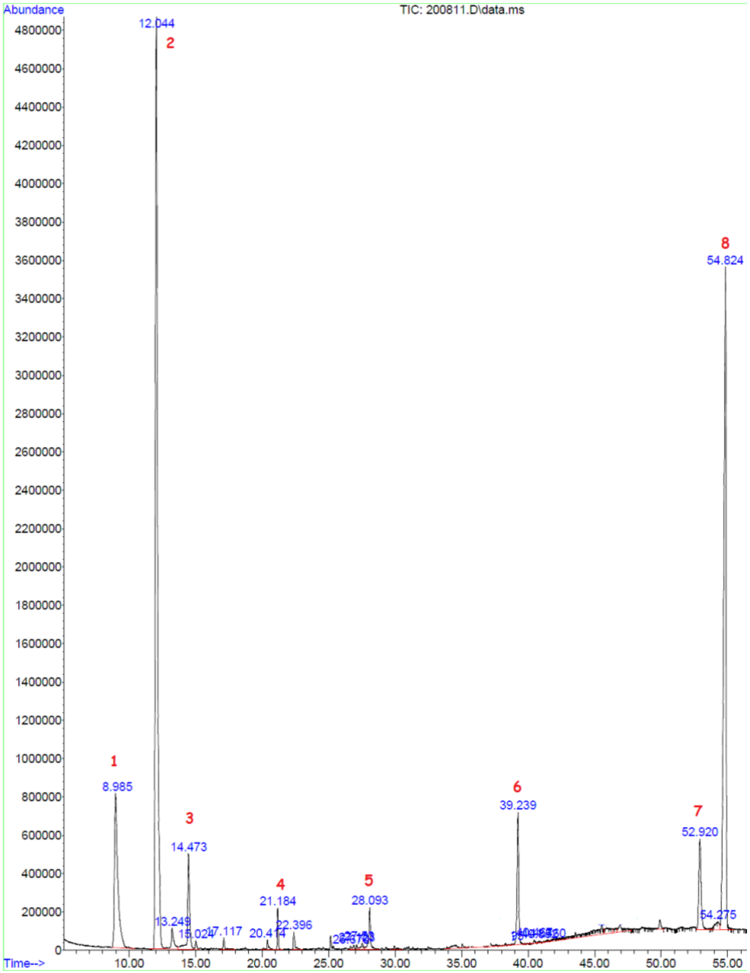

Fig. 1 Gas chromatogram of the reaction mixture of allylisothiocyanate and 2nd Grubbs catalyst after 1 h in DCM.[Grubbs catalyst] = 0.1mmol;[allylisothiocyanate]= 0.1 mmol; V = 10 ml

From the mass spectrum the peak appeared at 39.2 min was identified as thetargeted product SM1 with *m/z* value of 170.0 (Fig. 2).

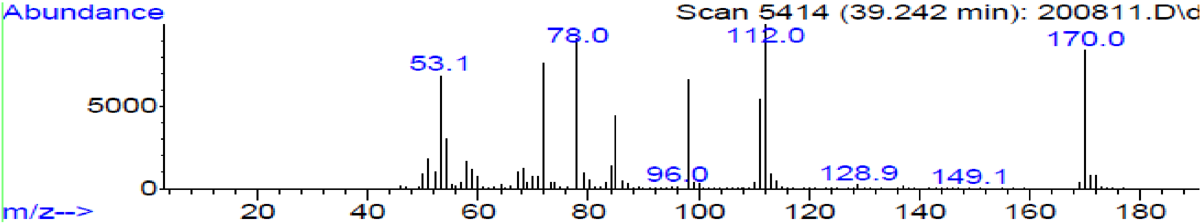

Fig. 2 Mass spectrum of 1,4-diisothiocyanatobut-ene(SM1)

The peaks at 8.9, 12.0 14.4, 28.0, 52.9 and 54.8 min were identified forstyrene (*m/z* 104.15g/mol), 1-isothiocyanatomethylstyrene (*m/z*175.25), tricyclohexylphosphine oxide (m/z 296.43) and tricyclohexylphosphine sulphide (m/z 312.49) respectively. Therefore, the isothiocyanato moiety showed its ability to interact with the central ruthenium in the catalytic system so as to disturb the pre-equilibrium step.The GC-MS analysis of the reaction mixture after 8 hreaction time showed two additional products. Five additional peaks were detected in the product after 24 h reaction time with the formation of1-isothiocyanatomethylstyrene(rt= 34.8 min) which is a cross-metathesis product of styrene and allylisothiocyanate.The two peaks for allylisothiocyanateis due to its isomerisation. The overall product analysis is shown in Table 1.

Table 1 GC-MS analysis of reaction products of self- metathesis of allylisothiocyanate reaction solution at different reaction times. [Grubbs catalyst] = 0.1mmol [allylisothiocyanate]= 0.1 mmol, V= 10 ml (rt)

Peak no.	1 h (rt/min, m/z,product)	8 h (rt/min, *m/z*, product)	24 h (rt/min, *m/z*, product)
1.	8.9g,104; styrene	8.6, 104; styrene	7.4, 104 ; styrene
2.	12.0, 99; AT	11.8, 99; AT	10. 99; AT
3.	14.2, 99; AT	14.4, 99; AT	13.2, 99; AT
4.	21.0 ni	21.0, ni	19.6, ni
5.	28, 135.2 ; PhNCS	27.9, ni	23.6,ni
6.	39.0, 170.0 ;SM1	39.1, 170.0, SM1	37.6, 170.0; SM1
7.	52.9, 296.4 ;$Cy_3P=O$	52.7, 296.4 ;$Cy_3P=O$	49.3, 296.4; $Cy_3P=O$
8.	54.8, 312.4, ;$Cy_3P=S$	54.5, 312.4; $Cy_3P=S$	50.9, 312.4 ; $Cy_3P=S$
9.	-	10.39, ni	9.0, ni
10.	-	13.0, ni	11.8, ni
11.	-	-	20.8, ni
12.	-	-	25.8, ni
13	-	-	32.7, ni
14.	-	-	34.8, 175; PhIMS
15	-	-	21.1, 107; CHClNCS
16	-	-	28.0, 231 ni
			40.7, 175 ni

Not important products are marked as not identified (ni)
SM1= 1,4-diisothiocyanatobut-ene; AT= allylisothiocyanate
PhIMS= phenylisothiocyanatostyrene
PhNCS= phenylisothiocyanate
CHClNCS= isothiocyanatochlorometane

Slight different in product retention times for the 24 h reaction time is due to slight change in the optimum operating conditions of the GC-MS spectrometer.

Cross metathesis with methyl oleate

Methyloleate can undergo a clean self and cross metathesis with several olefins meaning without the release of styrene and phosphine ligands from the catalytic pathway (Awang et al., 2016). Similarly the products of the cross metathesis of methyloleate with allylisothiocyanate can be designed as in Fig. 3 shown below.

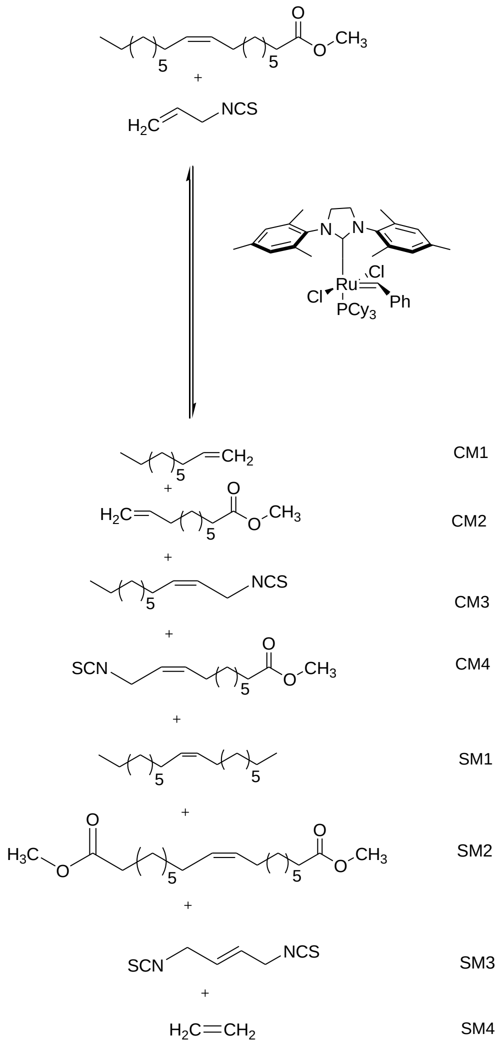

Fig. 3 Cross-metathesis of allylisothiocyanate with methyl oleate

The chromatogram of the reaction mixture after 1 h reaction time showed 17 major peaks together with several minor peaks (Fig. 4). As expected from the previous experiment the formation of styrene (rt= 8.9 min) and phosphine (rt= 52.9 and 54.8 min) were observed.

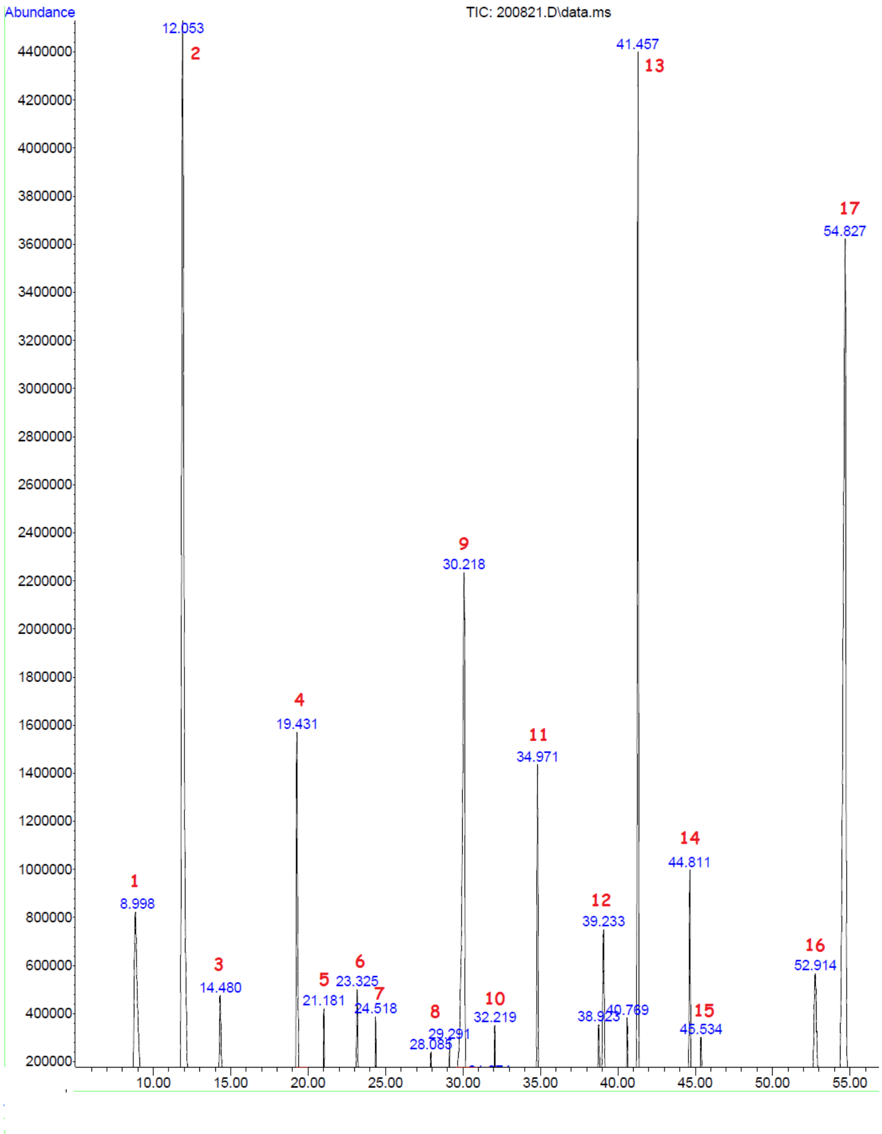

Fig. 4 Chromatogram of the reaction mixture of allylisothiocyanate with methyloleate after 1 h reaction time. [Grubbs catalyst] = 0.1mm; [allylisothiocyanate].= 0.1mm, [MO]= 0.1mmol, V = 10ml

The peaks at 12.0 and 41.4 min are for allylisothiocyanate and methyl oleate respectively. The targeted cross product methyl-11-isothiocyanatoundec-9-enoate (CM4) appeared at rt=38.9min with m/z = 255 (Fig. 5). The self-metathesis products SM1, SM2 and SM3 were clearly identified (Table 2).

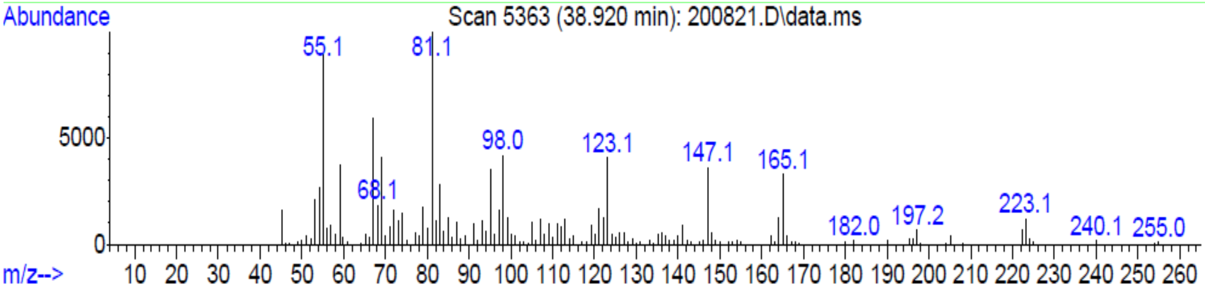

Fig. 5 Mass spectrum of metil-11-isothiocyanatoundec-9-enoate (CM4)

All the self- metathesis products SM1, SM2,and SM3 were present. The GC-MS of the reaction mixture after 24 h showed the presence of CM4 at 40.3 minbut with lesser amount than in 1 hour reaction. Small amount of CM3 was detected in the minor peaks of 42.2 min. The overall peaks from both reactions are given in Table 2.

Table 2 GC-MS analysis of reaction products of cross-metathesis of allylisothiocyanate and methyl oleate reaction solution at different reaction times. [Grubbs catalyst] = 0.1mmol [allylisothiocyanate]= 0.1mmol, V= 10 ml (rt)

Peak no.	1 h (rt/min, m/z, product)	24 h (rt/min, m/z, product)
1.	8.9, 104; styrene	7.4, 104; styrene
2.	12.0, 99 ; AT	10.9, 99 ; AT
3.	14.4, 99.1 AT	11.8, ni
4.	19.4, ni	13.2, 8.0, 99.1 AT
5.	21.1, ni	19.6, ni
6.	23.3, 252.4 ; SM1	20.8, ni
7.	24.5, ni	23.6, ni
8.	29.2, ni	26.4, ni
9.	30.2, ni	32.7, ni
10.	32.2, ni	37.6, ni
11.	34.9,296.4; MO	40.7 ,255.7 ; CM4
12.	39.2, 170.6 SM3	42.3, 211.3; CM3
13.	41.4, 255.7; CM4	49.3, 296.4; $Cy_3P=O$
14.	44.8, 340; SM2	50.9, 312; $Cy_3P=S$
15.	45.3 ni	-
16.	52.5, 296.4 $Cy_3P=O$	-
17.	54.8, 312.6 ; $Cy_3P=S$	-

Not important products are marked as not identified (ni).
SM1= octadec-9-ene; AT= allylisothiocyanate; MO= Methyl oleate;
SM2= dimethyloctadec-9-eneoate; SM3= 1, 4-diisothiocyanatobut-ene, CM3= 1-isothiocyanatoundec-2-ene; CM4= methyl-11-isothiocyanatoundec-9-enoate;
Slight different in product retention times for the 24 h reaction time is due to slight change in the optimum operating conditions of the GC-MS spectrometer.

Cross metathesis with ethyloleate

Ethyloleate has one extra carbon at the ester group is also expected to undergo cross metathesis with allylisothiocyanate in the same way as methyloleate (Fig. 6)

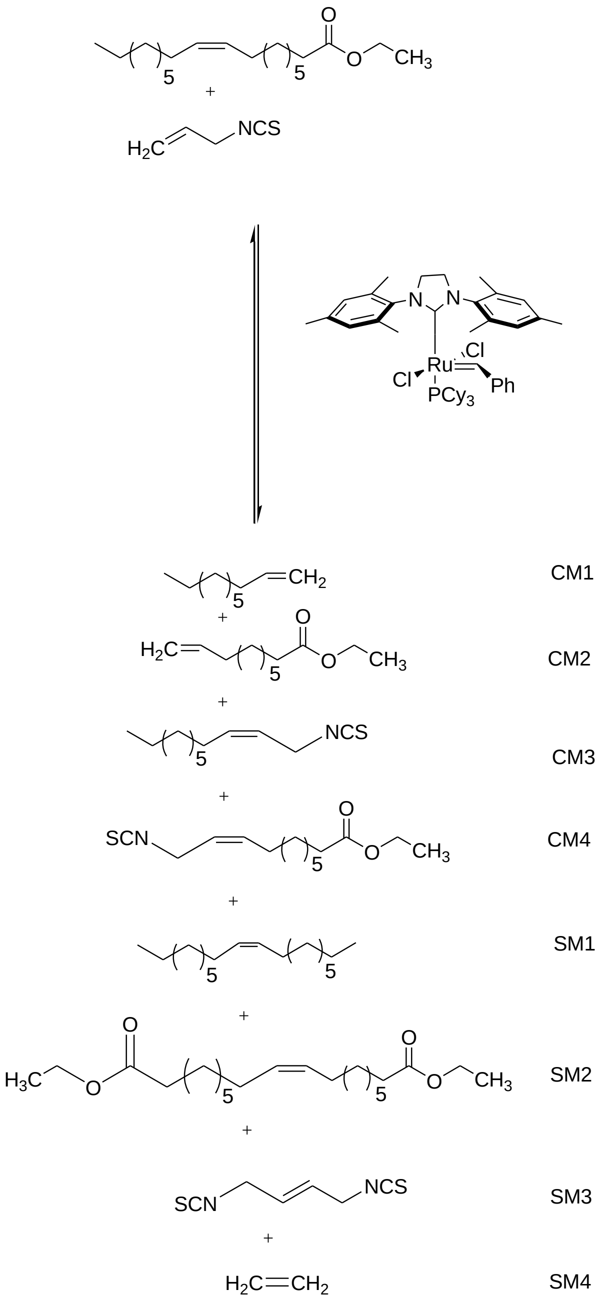

Fig. 6 Cross-metathesis of allylisothiocyanate and ethyl oleate

The chromatogram of the reaction mixture after 1 h reaction time shows 16 main and some minor peaks (Fig. 7).

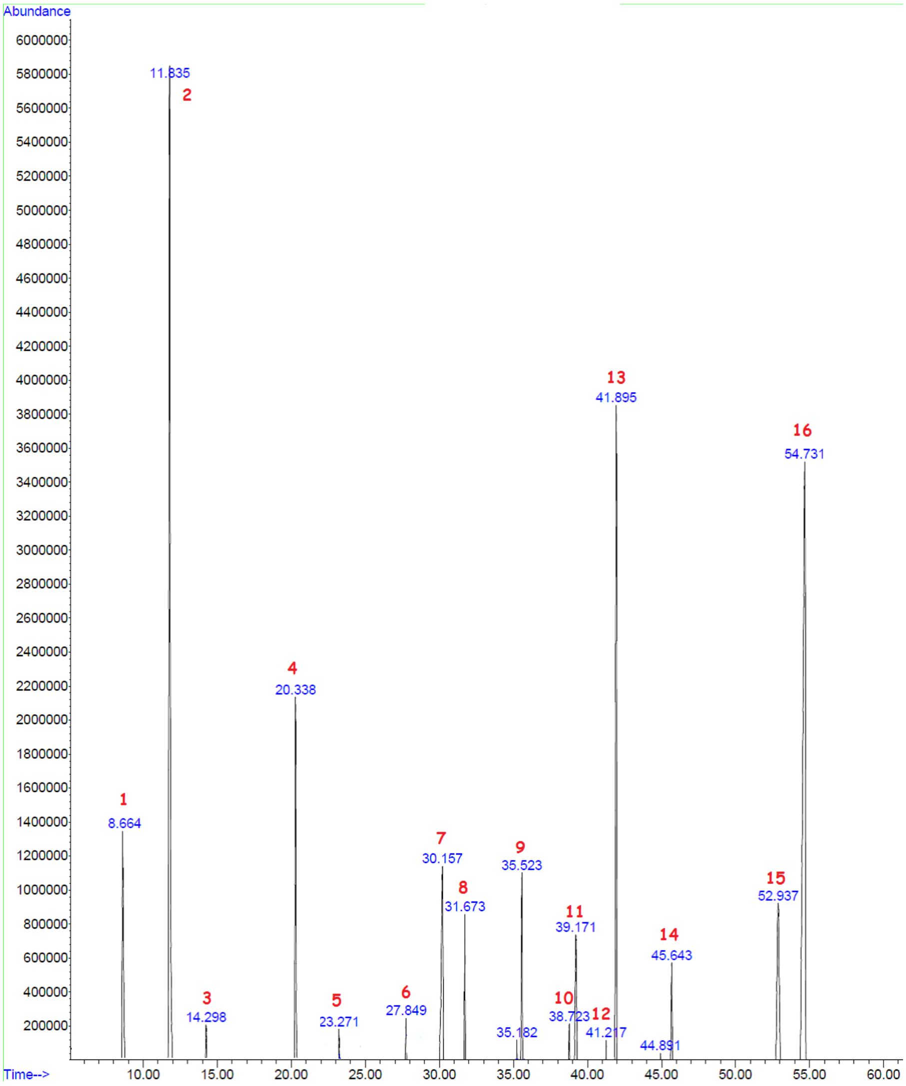

Fig. 7 Chromatogram of the reaction solution of allylisothicyanate and ethyl oleateafter 1 h reaction time. [Grubbs catalyst] = 0.1mm; [allylisothiocyanate] = 0.1mm 1, [EO]=0.1mmol, V= 10 ml

Peak no. 1, 2, 9, 15, and 16 are for styrene,allylisothicyanate, ethyl oleate, tricyclophosphine oxide and tricyclophosphine sulphiderespectively. Only two targeted cross product of CM3 (1-isothiocyanatoundec-2-ene) and CM4 (ethyl-11-isothiocyanatoundec-9-enoate) were detected togetherwith threeself-metathesis products ofSM1 (octadec-9-ene), SM2 (diethyloctadec-9-enoate) and SM3 (1, 4-diisothiocyanatobut-ene).The reaction solution after 24 h reaction also showed similar self and cross metathesis products (Table3).

SM1= octadec-9-ene; AT= allylisothiocyanate; EO= ethyl oleate;

SM2= diethyloctadec-9-eneoate; SM3= 1, 4-diisothiocyanatobut-ene, CM3= 1-isothiocyanatoundec-2-ene, CM4= ethyl-11-isothiocyanatoundec-9-enoate;

Slight different in product retention times for the 24 h reaction time is due to slight change in the optimum operating conditions of the GC-MS spectrometer.

Table 3 GC-MS analysis of reaction products of cross-metathesis of allylisothiocyanate and ethyl oleate reaction solution at different reaction times [Grubbs catalyst] = 0.1mmol [allylisothiocyanate]= 0.1mmol,V= 10 ml (rt)

Peak no.	1 h (rt/min, *m/z*)	24 h (rt/min, *m/z*)
1.	8.6, 104.4 styrene	7.41, 104.1 styrene
2.	11.8, 99; AT	10.5, 99 AT
3.	14.2,ni	11.4, ni
4.	20.3, 252.3; SM1	18.9, ni
5.	23.2, ni	19.6, ni
6.	27.8, ni	21.8, 252.3; SM1
7.	301. ni	23.8, 210.2: ni
8.	31.6, 176.6; SM3	26.4, ni
9.	35.5, 310.5; E0	28.6, 211.4 ;CM3
10.	38.7, ni	30.2, ni
11.	39.7,ni	31.1,ni
12.	41.8, 269 ; CM4	34.6, 310.5 ; EO
13.	41.8, ni	37.7, ni
14.	45.6, 340; SM2	40.7, 269; CM4
15.	52.9, 296 $Cy_3P=O$	44.0, 340; SM2
16	54,7, 18.2, 312.4; $Cy_3P=S$	49.3, 296; $Cy_3P=O$
17	-	50.7, 312.4; $Cy_3P=S$

Not important products are marked as not identified (ni).

Cross metathesis with ethyllinoleate

Preliminary study on the self-metathesis of ethyl linoleatehaving two double bonds at position 9 and 12 was complicated.On the other hand, self-metathesis of methyl linoleate by WCl_6-$SnMe_4$ catalyst has been reported to give alkene, cyclohexadiene, monoesters and diesters (Yarmo et al., 1992).Despite the complication the product design on the cross metathesis with allylisothiocyanate can always be worked out as shown in Fig. 8.

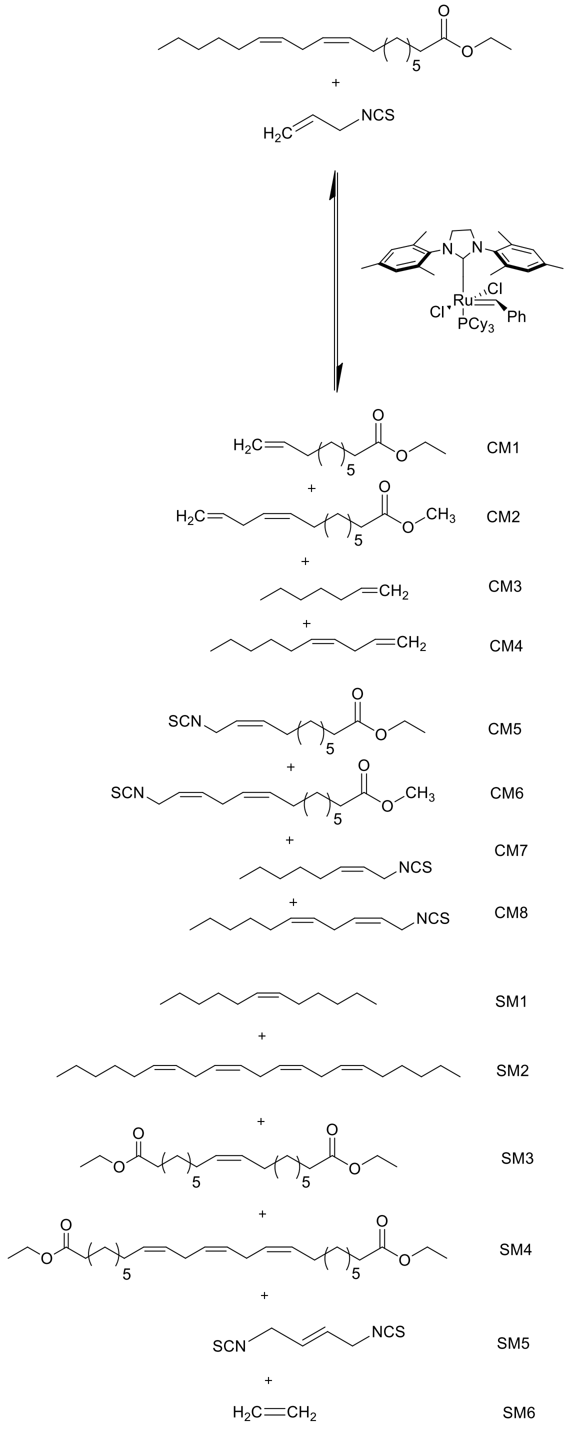

Fig. 8 Cross- metathesis of allylisothiocyanate with ethyllinoleate

Surprisingly, despite the complicated nature of the self-metathesis of ethyllinoleate the cross metathesis with allylisothiocyanate could still show the formation of some targeted products together with the styrene and phosphine oxide/sulfide. GC-MS of the reaction solution after 1 h reaction time showed at least 12 major peaks (Fig.9) corresponding to allylisothiocyanate, ethyllinoleate, styrene, tricyclohexylphosphine oxide, tricyclohexylphosphinesulfide, 1,4-diisothiocyanatobut-2-ene(SM5), and 1-isothiocyanatooct-2-ene (CM7) were detected from the mass spectra.

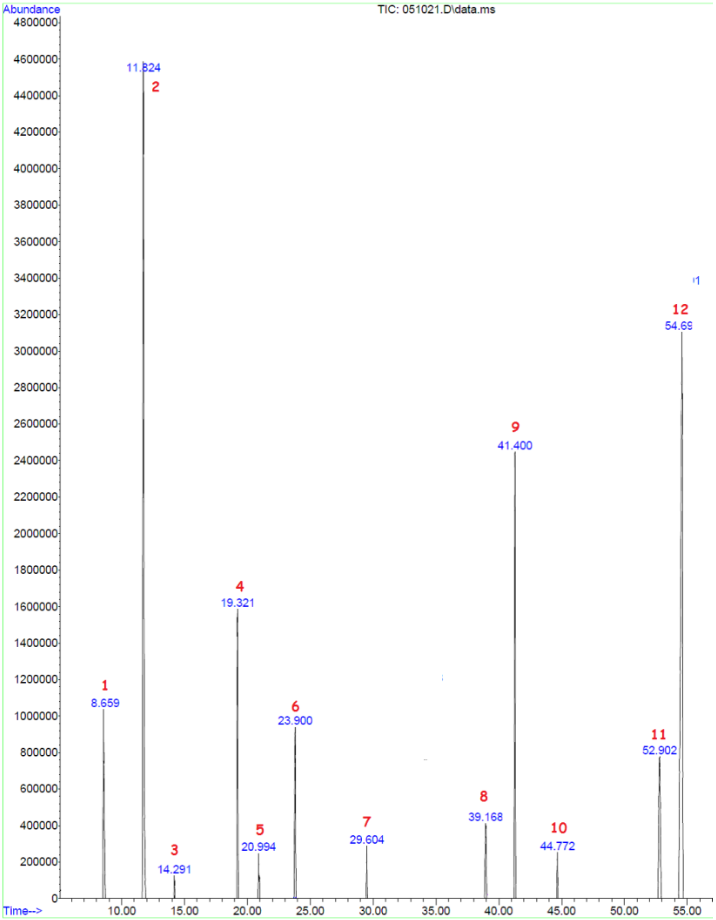

Fig. 9 Gas Chromatogram of reaction solution ofallylisothiocyanate and ethyl linoleate at 1 h reaction time [Grubbs catalyst] = 0.1mmol; [allylisothiocyanate]= 0.1mmol; [linoleate]=0.1mmmol; V=10ml

The dodec-6-ene (SM4) and 1-isothiocyanatomethylstyrenewere detected from the minor peaks. GC-MS spectrum of the reaction mixture after 24 h reaction time showed more targeted products of CM1, CM2 and CM3 together with self-metathesis of SM1 and SM4 (Fig. 9). The overall products identified are given in Table 4.

Table 4 GC-MS analysis of reaction products of cross-metathesis of allylisothiocyanate and ethyl linoleate reaction solution at different reaction times. [Grubbs catalyst] = 0.1mmol [allylisothiocyanate]= 0.1mmol; [EL] V= 10 ml(rt)

Peak no.	1 h (rt/min, %, m/z)	24 h (rt/min, %, m/z)
1.	8.6, 104.1; styrene	6.9, 168.2
2.	11.8, , 99; AT	16.1, ni
3.	14.2, ni	18.9, ni
4.	19.4, ni	21.8, ni
5.	20.9, ni	22.4, 169 ; CM7
6.	23.9, 169 ; CM7	23.8, ni
7.	29.6, ni	26.2, ni
8.	39.1, 170; SM5	28.9, ni
9.	41.4, ni	29.6, ni
10.	44.7, ni	31.2, ni
11.	52.9, 296 $Cy_3P=O$	34.7, 308; EL
12.	54.6, 312; $Cy_3P=S$	37.7, 170; SM5
13.		40.7, ni
15.	-	44.0, ni
16.	‘	45.1, ni
17.	-	49.5, ni
18.	-	50.7, 312; $Cy_3P=S$

Not important products are marked as not identified (ni)

AT= allylisothiocyanate; EL= ethyllinoleate; SM1= octadec-9-ene, SM5= diisothiocyanatobut-2-ene; CM7=1-isothiocyanatoocta-2-ene

CONCLUSION

Despite the release of styrene and the formation of tricyclohexylfosfin oxide and tricyclohexylfosfin sulphide from the preliminary catalytic cycle the self-metathesis of both allylisothiocyanate and alkyl esters (methyloleate, ethyloleate and ethyl linoleate) took place without the formation of metallic ruthenium or ruthenium oxide. Cross metathesis of allylisothiocyanate with all the esters also gave the self and targeted cross products. Therefore preventing the release of styrene and phosphine from the system is the next challenge by applying a suitable protecting agent. Further work on this aspect is on progress in collaboration with Prof. Nomura Group at Tokyo Metropolitan University, Tokyo.

Author Contribution Statement Bohari M Yaminis the group leader and conceived the idea, and edited the manuscript. Sara Maira M. Hizamwas the master student who conducted the experiments and wrote the manuscript. Nor WahidaAwang was a PhD student working in the group on related subject. SitiAishahHasbullah is the co-supervisor in the project.

Conflict of Interests All the authors have approved the final version being submitted. The article is an original work and has not been submitted anywhere else. The authors declare that there is no conflict of interest.

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