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PAPER

Application of a metathesis reaction in the synthesis of sterically congested medium-sized rings. A direct ring closing *versus* a double bond migration–ring closing process†

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An efficient double bond migration–ring closing metathesis reaction leading to cycloheptene derivatives is observed when specific sterically congested 1,9-dienes are treated with the Grubbs' imidazolidene ruthenium catalyst. The simultaneous use of the Grubbs' catalyst and RuClH(CO)(PPh$_3$)$_3$ facilitates the tandem bond migration–metathesis process. RuClH(CO)(PPh$_3$)$_3$ alone is capable of triggering an unactivated double bond migration that may have preparative applications.

Introduction

In a work directed at the total synthesis of diterpenoids with the dicyclopenta[*a,d*]cyclooctane carbon skeleton (5-8-5), such as in cycloaraneozene and epoxydictymene (Fig. 1, **1** and **2**, respectively), we envisaged the construction of key cyclopenta-cyclooctane intermediate **4** by a ring closing metathesis (RCM) reaction with diene **3**. A mono- and a di-substituted double bond in a relative 1,9-position would be involved in this process. The closing of an eight-membered ring was, generally, considered to be a difficult reaction.[1–6] However, some encouraging examples of the application of metathesis in the synthesis of complex cyclooctene derivatives have been reported[7–16] (more recent related examples are also noteworthy[17–20]). The distinctive feature of substrate **3** was the *l,l* relative configuration around C-2,C-1′ and C-1′,C-2′ as well as the presence of a bulky *S-tert*-butylthiocarbonyl group in a position adjacent to the cyclopentane ring. The ring closing process would place this group in a pseudo-axial position and create considerable steric congestion.

Diene **3** exposed to the Grubbs' imidazolidene ruthenium catalyst (**7**, Fig. 2) in refluxing benzene afforded a RCM reaction product in a 60–70% yield. Surprisingly, the product was not the expected cyclooctacyclopentane **4** but the hydroazulene derivative **5**. In an alternative attempt, the treatment of **3** with Grubbs' benzylidene catalyst **6** in refluxing dichloromethane led to a mixture of bimolecular cross metathesis products ("dimers", 87%), which on heating with **7** in dichloroethane generated the same product, **5** (49%). It was evident that the propene was the complementary product of the formation of **5** from **3** and that a double bond migration preceded the metathesis.
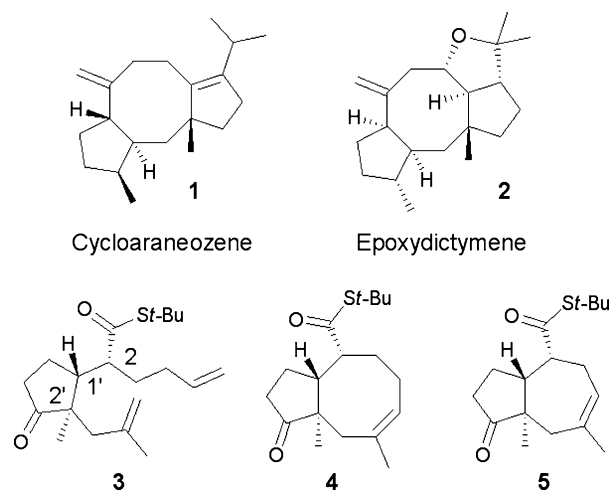
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Fig. 1 The target natural products (**1**, **2**), intermediate diene **3**, the expected RCM product, **4**, and obtained hydroazulene derivative **5**.

Tandem double bond migration–RCM reactions have been scarcely reported in the literature (the previously reported observations on a double bond migration related to a metathesis will be discussed later). In order to clarify the structural features that may be promoting the tandem process, selected dienes analogous to **3** were synthesized and their transformation with Grubbs' ruthenium catalysts were studied. Additionally, a simultaneous action of catalyst **7** and known ruthenium double bond migration catalyst[21–22] **9** was scrutinized. A preliminary communication on our findings was previously published.[23–24] Herein, we present a complete account of the work.

Results

The metathesis of **3** and four related 1,9-dienes, **10–13**, (Fig. 3), with a di-substituted double bond in the "lower" side chain, was examined using catalyst **7** alone or a mixture of catalysts **7** and

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Fig. 2 The catalysts used in the present work.

Fig. 3 The metathesis of dienes with a di-substituted double bond in the lower side chain, bearing a *S-tert*-butylthiocarbonyl group: substrates and products.

9. Additionally, the metathesis of diene **14**, devoid of the angular methyl and differing from **3** by the relative configuration, was tested (for the synthesis of substrates *vide infra*).

Heating of **3** in benzene, at reflux, in the presence of catalyst **7** (5 mol%), for 16–72 h afforded azulene derivative **5** in 49–56% yield (Table 1, entry 1). The outcome of the reaction was not affected by additives that were reported to inhibit double bond migration, such as tricyclohexylphosphine oxide,[25] (5 mol%), or 1,4-benzoquinone,[26] (10 mol%) or by using 1,2-dichloroethane as the solvent[25] (entry 2). The catalyst **8**[27] was found to be less effective, although some migration–metathesis product was also formed (entry 3). The reaction carried out in the presence of **7** (5 mol%) with ruthenium hydride catalyst **9** (1 mol%) subsequently added, afforded product **5** in 84% yield (entry 4). The increase in the amount of catalyst **9** to 5 mol% resulted in a quantitative conversion of the substrate to product **5** (entry 5). Interestingly, briefly preheating catalysts **7** and **9** (5 mol% each), before the substrate was added, had a negative effect on the product yield (65%, entry 6).

As anticipated, 1,8-diene **10**, with the double bond in the C-4,C-5 position, in the presence of the catalyst **7**, in refluxing benzene, smoothly afforded product **5** (98% yield, entry 7). The substrate **11**, with the upper side chain extended by a methylene group, and catalys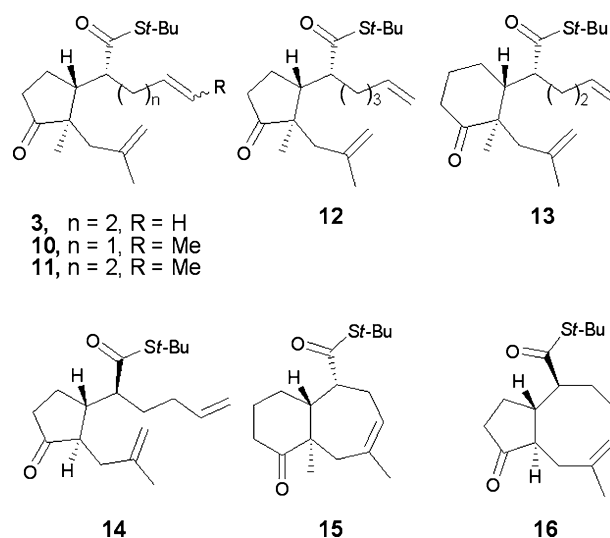t **7**, heated in benzene, afforded a mixture of two products that were separated by column chromatography. The product isolated in a 34% yield was identified as the hydroazulene derivative **5**. The HRMS, ^{1}H, and ^{13}C NMR spectra of the second product (40% yield) unambiguously pointed to the cyclooctene structure **4** (entry 8). Heating of **11** with the catalysts **7** and **9** (5 mol% each) exclusively provided **5** (86%, entry 9).

1,10-Diene **12** and the catalyst **7** afforded a small amount of **5** (17% yield) with dimers prevailing (66% yield; entry 10). The reaction of substrate **12** with the mixture of catalysts **7** and **9** (5 mol% each) afforded **5** in a substantially higher yield (64%), along with dimers, 30% yield (entry 11).

The 6-membered ring substrate **13**, under the standard metathesis conditions with the catalyst **7** (5 mol%), gave the corresponding cycloheptene derivative **15**, in 57% yield (entry 12). Finally, heating of **14** and the catalyst **7** in benzene at reflux for 16 h gave a single product that was identified as the cyclooctene derivative **16** (58% yield; entry 13).

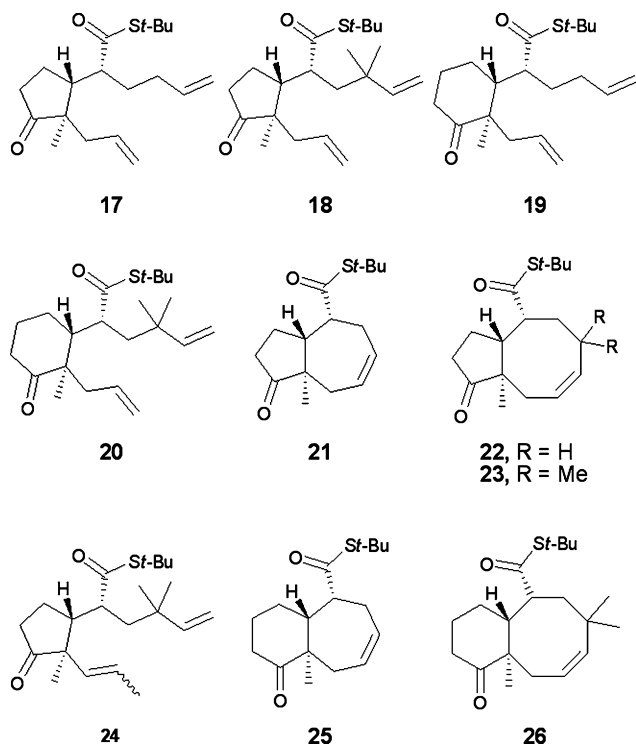**Table 1** The metathesis of dienes with one di-substituted double bond and a *S-tert*-butylthiocarbonyl group

| Entry | Diene | Catalyst (5 mol%) | Catalyst 9, (mol%) | Solvent[a] | Time, h | Products, yield (%) | | |
						7-memb.	8-memb.	dimers
1	3	7[b]	—	C6H6	16–72	5, 49–56		
2	3	7	—	(CH2Cl)2	72	5, 67		
3	3	8	—	C6H6	24	5, 15		
4	3	7	1	C6H6	6	5, 84		
5	3	7	5	C6H6	6	5, 100		
6	3	7[c]	5	C6H6	6	5, 65		
7	10	7	—	C6H6	2	5, 98		
8	11	7	—	C6H6	72	5, 34	4, 40	
9	11	7	5	C6H6	24	5, 86		
10	12	7	—	C6H6	72	5, 17		66
11	12	7	5	C6H6	24	5, 64		30
12	13	7	—	C6H6	16	15, 57		
13	14	7	—	C6H6	16		16, 58	

[a] All reactions were carried out at reflux temperature. [b] Addition of Cy3PO or 1,4-benzoquinone didn't change the reaction outcome. [c] A mixture of the catalysts was preheated (30 min) before the substrate was added.

Table 2 The metathesis of 1,9-dienes with two mono-substituted double bonds and a *S-tert*-butylthiocarbonyl group (in benzene at reflux temperature)

Entry	Diene	Catalyst (5 mol%)	Catalyst 9, (mol%)	Time, h	Products, yield (%)		
					7-memb.	8-memb.	other
1	17	6, 10	—	72	21, 40–49	22, *ca.*15	
2	17	7, 5	5	2	21, 38		
3	18	7, 10	—	72		23, 52	
4	18	7, 5	5	16		23, 15	24, 34
5	19	7, 5	—	16	25, 42		
6	20	7, 5	—	15		26, 30	

After establishing that the tandem reaction is not a one-substrate artefact, we turned our attention to the dienes in which both double bonds are mono-substituted. Heating of diene **17** (Fig. 4) in benzene in the presence of the catalyst **7** (10 mol%) led to at least five products, with one dominating the mixture. None of these products could be isolated in a pure form by column chromatography. However, HPLC-MS analysis of the mixture and the ^{1}H and ^{13}C NMR spectra of the mixture enriched with the main product (column chromatography) pointed to the hydroazulene structure **21**. The yield of this product was estimated to be 40–49%. Another product was identified by HPLC-MS analysis as cyclopentacyclooctene **22** and its content was estimated to be 15% (Table 2, entry 1).

17   **18**   **19**

20   **21**   **22**, R = H   **23**, R = Me

24   **25**   **26**

Fig. 4 The metathesis of dienes with a mono-substituted double bond in the lower side chain, bearing a *S-tert*-butylthiocarbonyl group: substrates and products.

The consumption of **17** in the presence of the both catalysts, **7** and **9**, was relatively fast. However, no improvement in the product yield was noted (entry 2).

The diene with the blocked allylic position in the upper side chain (**18**), under analogous conditions, afforded the cyclooctene

derivative **23** in 52% yield, along with some dimeric products (entry 3). It should be noted that placing one of the double bonds in a neopentyl position considerably slows the reaction down (the respective derivative of **3** did not cyclize at a reasonable rate). On heating of **18** in the presence of both catalysts (**7** and **9**) the derivative **23** (15% yield) and diene **24** (34% yield), were obtained (entry 4). The latter product results from the migration of the double bond in the lower side chain.

Diene **19** and catalyst **7** afforded a product with cyclohexacyclo-heptene rings (6,7), **25** (42% yield; Table 2, entry 5). This product was somewhat easier to purify than its hydroazulene analogue, as discussed earlier. The reaction of the *gem*-dimethyl diene **20** afforded **26** in 30% yield (Table 2, entry 6).

Substrates with a methoxycarbonyl group instead of a *S-tert*-butylthiocarbonyl group were examined next (Fig. 5). Diene **27** with the *l,l* relative configuration and with one di- and one mono-substituted double bond, with catalyst **7**, in refluxing benzene, underwent a bond migration–RCM reaction to afford the azulene derivative **32** in 85% yield (Table 3, entry 1). An analogous experiment with olefin isomerization catalyst **9** (5 mol%) added afforded the same product, but the yield was higher and the substrate was consumed in a shorter time (entry 2). Curiously, when 1 mol% of catalyst **9** was added, **32** was accompanied by the eight-membered ring product **33** (entry 3). The substrate with the blocked allylic position in the upper side chain (**28**) only afforded dimers (entry 4).

Diene **29**, with the *u,l* relative configuration, smoothly underwent ring closing to afford the cyclooctene derivative **34** in 96% yield (entry 5).

Diene **30**, with two mono-substituted double bonds (*l,l* relative configuration), on treatment with catalyst **6** in benzene afforded the product of an isomerization–RCM reaction, **35** (56% yield; entry 6). When both metathesis (**7**) and isomerization (**9**) catalysts were present, the substrate was consumed in a markedly shorter time, but the product yield was lower (entry 7).

Finally, diene **31**, with two mono-substituted double bonds and the *u,l* relative configuration, in the presence of catalyst **6** in dichloromethane smoothly afforded the cyclooctene product **36** (94% yield, entry 8).

In the concluding part of our studies, we examined di-mono-substituted 1,9-dienes with a hydroxymethyl group instead of an ester group. Since the literature data concerning the effect of a free hydroxy group on the methathetic formation of medium-size rings appeared contradictory, with both the enhancement as well as the inhibition of the reaction rate reported,[28–30] the respective benzoates were also examined.

Alcohol **37** and catalyst **6** (3 mol%) afforded cyclooctene derivative **41** in 47% yield (Fig. 6, Table 4, entry 1). The

Table 3 Metathesis of 1,9-dienes bearing a methoxycarbonyl group

Entry	Diene	Catalyst (mol%)	Catalyst 9, (mol%)	Solvent	Time, h	Products, yield (%)		
						7-memb.	8-memb.	other
1	27	7(5)	—	C_6H_6	16	32, 85		
2	27	7(5)	5	C_6H_6	0.5	32, 94		
3	27	7(5)	1	C_6H_6	6	32, 38	33, 36	
4	28	7(10)	—	C_6H_6	72			dimer, 83
5	29	7(3)	—	CH_2Cl_2	6		34, 96	
6	30	6(3)	—	C_6H_6	72	35, 56		
7	30	7(5)	5	C_6H_6	6	35, 28		
8	31	6(3)	—	CH_2Cl_2	16		36, 94	
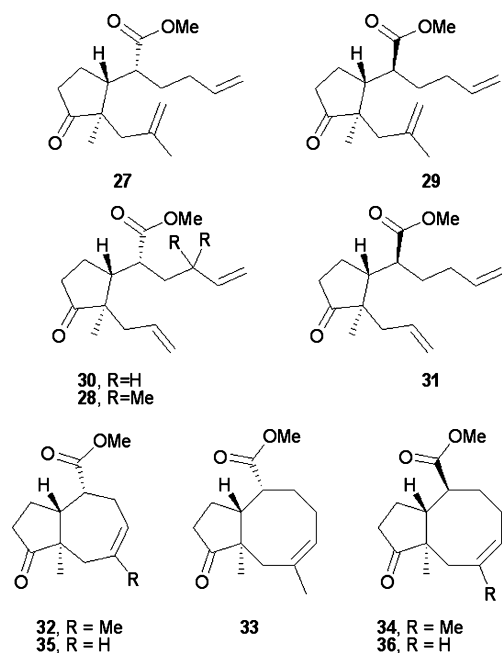
Fig. 5 The metathesis of dienes bearing a methoxycarbonyl group: substrates and products.
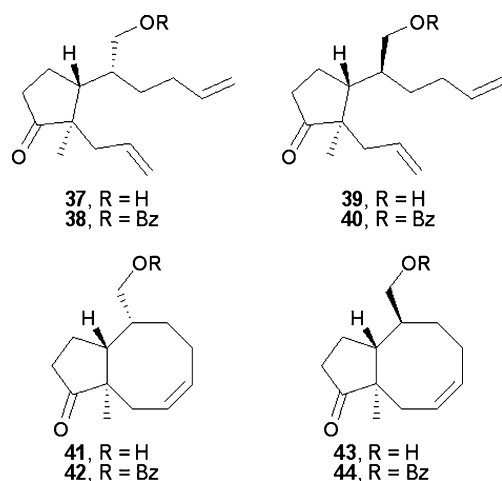
Fig. 6 The metathesis of 1,9-dienes with di-mono-substituted double bonds, bearing no ester function: substrates and products.

corresponding benzoate **38**, under analogous reaction conditions gave **42** in 18% yield (entry 2). Hydroxy diene **39**, with the

Table 4 The metathesis of 1,9-dienes bearing a hydroxymethyl or benzoxymethyl group using catalyst **6** (3 mol%)

Entry	Diene	Solvent	Time, h	Product, yield (%)
1	37	C_6H_6	72	41, 47
2	38	C_6H_6	72	42, 18
3	39	CH_2Cl_2	16	43, 99
4	40	CH_2Cl_2	16	44, 99

l,u configuration, underwent the RCM reaction in refluxing dichloromethane to afford cyclooctene derivative **43** in a 99% yield (entry 3). Analogously, benzoate **40** was transformed into **44** in a virtually quantitative yield (entry 4).

The metathesis reaction: discussion

The ruthenium metathesis catalysts and related ruthenium-containing species are capable of triggering the migration of unactivated double bonds, either during the reaction, or during the product isolation procedure (for example, distillation).[31–35]

The double bond migration that occurs prior to the metathesis was observed during metathetic macrocyclization with use of the Nolan–Grubbs catalyst[36–38] (an analogous process was observed in the presence of a molybdenum catalyst[8]). A linear 1,9-diene bearing free hydroxy groups, in the presence of catalyst **6**, afforded a mixture of eight- and seven-membered ring products, the latter arising from a double bond migration–metathesis process.[14] More recently, the cyclization of complex 1,9-dienes to form a "contracted" 7-membered ring has also been reported.[20,39]

The transformation of an allylic alcohol into a ketone with one fewer carbons, under the conditions of metathesis in the presence of catalyst **6**, was noted.[40] In some specific cases, the attempted RCM reaction was hampered by a double bond shift, leading to the product being resistant to further changes.[18,20,41]

In a broadly accepted explanation of the double bond migration mechanism,[35,42] the ruthenium hydride species, contaminating the catalyst or generated from the catalyst in the reaction mixture, brings about the successive hydroruthenation–ruthenium hydride elimination sequences.

In contrast to the esoteric ruthenium hydrides that possibly accompany the metathesis catalysts, the well-defined, easily accessible, ruthenium hydride complexes are used to isomerize allyl ethers into vinyl ethers or allyl amines into vinyl amines under mild conditions.[21,43–45] Ruthenium hydride **9** is one of the most efficient and convenient isomerization catalysts. A consecutive, but separate use of metathesis catalyst **6** and then catalyst **9**,

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provided an efficient route to various benzo-fused heterocycles.[46,47] Catalyst **7** was modified by treatment with a mixture of H_2–N_2 for the tandem metathesis–double bond migration process leading to cyclic enol ethers.[48,49] However, the simultaneous use of metathesis and isomerization catalysts has not been reported in the literature, to the best of our knowledge.[50]

We found that all three ruthenium metathesis catalysts (**6**, **7**, **8**) were capable of initiating the bond migration–metathesis of a series of 1,9-dienes related to 1-allyl-2-(pent-4-enyl)cyclopentane, although catalyst **8** gave a low yield of products. The catalyst **7** was the most efficient for both types of dienes, with one di-substituted double bond and two-mono-substituted double bonds.

The *gem*-dimethyl derivatives **18** and **20**, for which the upper side chain double bond migration is blocked, underwent metathesis with catalyst **7** to give cyclooctene derivatives, **23** and **26**, respectively (52% and 30% yield) along with the corresponding dimers. The diene **28** gave only a mixture of dimers. The high degree of steric congestion of the formed cyclooctane derivatives is noteworthy.

The "normal" RCM leading to the cyclooctane derivatives, as the major product or a side product, was observed for the following 1,9-dienes: **11**, **14**, **17**, **18**, **20**, **29**, **31**, **37–40**. Tandem double bond migration–metathesis reactions occurred when the following eight substrates were used: **3**, **11–13**, **17**, **19**, **27** and **30**.

In the bond migration–metathesis process, the formation of seven-membered ring derivatives appears to be favoured, since product **5** is formed from the various substrates: **3** (single migration of the double bond), **10** ("direct"), and **12** (two-fold migration of the double bond). No annulation with formation of a six-membered ring was recorded.

Analysis of the structural features of the substrates leads to the generalizations illustrated in Scheme 1. The tandem bond migration–rearrangement was only observed for substrates bearing an alkylthio- or alkoxycarbonyl group [–C(O)X] attached at position 2.
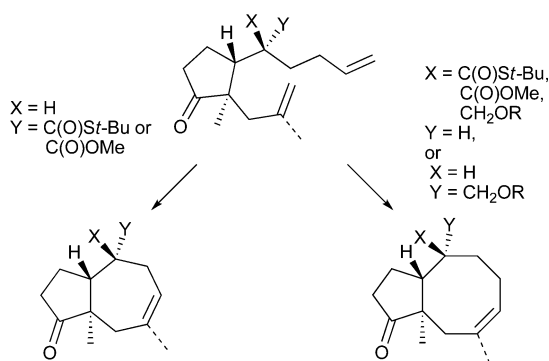
Scheme 1 The structural features relevant to the bond migration–metathesis or "direct" metathesis induced by catalyst **7**.

The stereogenic centers in a *l,l* relative configuration (substituent at C-2 in a pro-axial orientation) are essential for the tandem migration–metathesis sequence. The relative configuration effect is particularly revealing when the reaction outcomes for epimer pairs **27–29** and **30**, **31** are compared.

The bond migration–metathesis process was observed for substrates with both di- and mono-substituted double bonds in the lower side chain. However, substrates with a mono-

Table 5 Bond migration–metathesis of dienes with catalyst **7** alone or with a mixture of catalysts **7** and **9** (products, % yields)

Catalyst	Substrate				
	3	**11**	**12**	**27**	**17**
7	**5**, 67	**5**, 34	**5**, 17	**32**, 85	**21**, 49
7 and **9**	**5**, 100	**5**, 86	**5**, 64	**32**, 94	**21**, 38

substituted double bond, in general, afforded products that were more difficult to purify and in lower yields. The difference likely reflects the possibility of further involvement of the initially formed bicyclic products with disubstituted double bonds (as in **21**) in the metathesis and/or double bond migration processes, whereas products with trisubstituted double bonds (as **5**) are removed from the reaction cycle.

Some additional comments on the simultaneous use of metathesis and isomerization catalysts are in order. A joint application of catalysts **7** and **9** was effective in generating contracted ring products with respect to substrates **3**, **11**, **12**, **27** with a di-substituted double bond. However, no positive effect was observed with diene **17** (mono-substituted double bond) (Table 5).

It should be noted that the formation of hydroazulene **5** from **11** occurred through the migration of an "internal" double bond. 1,10-diene **12** underwent "two-fold" double bond migration, presumably *via* **11**.

The use of catalysts **7** and **9** with diene **18** afforded a product of double bond migration in the lower side chain. Another example of unactivated bond migration induced by catalyst **9** is discussed in the section devoted to the preparation of substrates (compound **10**), possibly indicating a broader synthetic application of this catalyst.

Various aspects of non-bonding interactions were considered for both the reaction products as well as the intermediates in an effort to explain the noted preference of the isomerization–cyclization reaction. A comparison of the molecular models of the seven- and eight-membered ring products, for example **5** and **4**, suggested only a minor difference in their steric strain.

Inspection of molecular models of the reaction intermediates with a ruthenium-containing four membered ring suggested that the formation of a seven-membered ring requires less non-bonding interactions, but no conclusive prediction could be made.

The synthesis of dienes for metathesis studies

The substrates with a *l,l* configuration were prepared by starting from 2-methylcyclopent-2-en-1-one (**49**, Scheme 2), 2-methylcyclohex-2-en-1-one (**50**), or methylcyclopent-2-en-1-one (**54**), the respective ketene acetals (**45–48**) and allyl (2-methylprop-2-enyl) methyl carbonates (**52** and **53**, respectively), using the tandem Mukaiyama–Michael addition and Tsuji alkylation reactions. The unsaturated ketone was first treated with ketene acetal in dichloromethane (DCM), at −78 °C, in the presence of trimethylsilyl triflate (5 mol%), to afford trimethylsilyl enol ethers **51**. These intermediates were isolated by a quick filtration of the reaction mixture through a pad of silica gel and evaporation. The NMR analysis of these products indicated that the virtually pure (*like*) diastereomers were formed. Trimethylsilyl triflate was found to be the catalyst of choice for this reaction, since it could be easily removed from the reaction mixture before the subsequent step.[51,52]
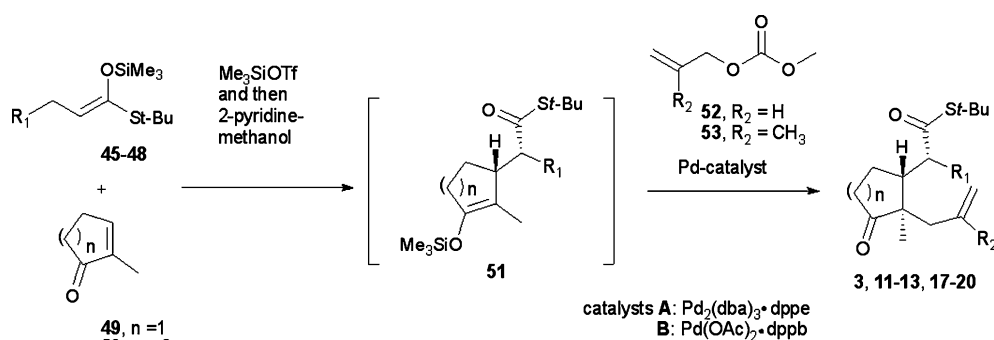
Scheme 2 Syntheses of dienes **3**, **11–13** and **17–20**.

Table 6 Synthesis of dienes **3**, **11–13** and **17–20**

Entry	Substrates, n, R^1	Allylation reaction R^2, catalysts	Product, yield (%)
1	1, –CH₂CH=CH₂ (**45**)	H, **A**	**17**, 68
2	1, –CMe₂CH=CH₂ (**46**)	H, **A**	**18**, 69
3	2, –CH₂CH=CH₂ (**45**)	H, **A**	**19**, 69
4	2, –CMe₂CH=CH₂ (**46**)	H, **A**	**20**, 62
5	1, –CH₂CH=CH₂ (**45**)	CH_3, **B**	**3**, 86
6	1, –CH₂CH₂CH=CH₂ (**47**)	CH_3, **B**	**12**, 39
7	1, –CH₂CH=CH₂CH₃ (**48**)	CH_3, **B**	**11**, 64
8	2, –CH₂CH=CH₂ (**45**)	CH_3, **B**	**13**, 22

Table 7 The preparation of methyl esters **27–31**

				Product, yield (%)	
Entry	R^1	R^2	Thioester	u,l	l,l
1	CH₃	H	**3**	**29**, 45–49	**27**, 40–42
2	H	H	**17**	**31**, 46	**30**, 42
3	H	CH₃	**18**		**28**, 82

Upon the use of trityl hexachloroantimonate (TrSbCl₆), which is the generally preferred catalyst for the Mukaiyama addition,[53] the reproducibility of the tandem process yield was problematic.

The silyl enol ethers were, without purification, subjected to the reaction with allyl methyl carbonate (**52**) or methyl 2-methylprop-2-enyl (methallyl) carbonate (**53**) and a suitable palladium catalyst. With the former, the classic palladium dibenzylacetone complex [Pd₂(dba)₃]-1,2-(diphenylphosphine)ethane (dppe) was used.[54,55] The reaction with methallyl methyl carbonate (**53**) was carried out in the presence of a modified catalyst consisting of palladium acetate and 1,4-(diphenylphosphine)butane (dppb). The results of these reactions are summarized in Table 6.
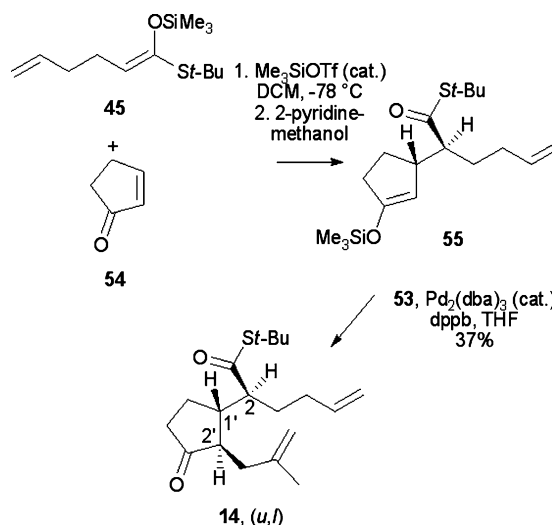
The synthesis of thioester **14** was accomplished essentially using the reported procedures for the conjugate addition step and the procedure developed earlier for the allylation step (Scheme 3). It is well-documented that when cyclopent-2-en-1-one (**54**) is used as the acceptor in the Mukaiyama–Michael addition, products with a u,l configuration are formed,[53] in contrast to the reactions discussed earlier involving 2-methyl-cyclopent-2-en-1-one (**49**).

Diene **10** was prepared by treatment of **3** with the ruthenium hydride catalyst **9** (1 mol%) in benzene at reflux temperature for 10 min, followed by chromatography. The product was isolated in a 87% yield as a mixture of E and Z isomers, ca. 3 : 1 (Scheme 4).
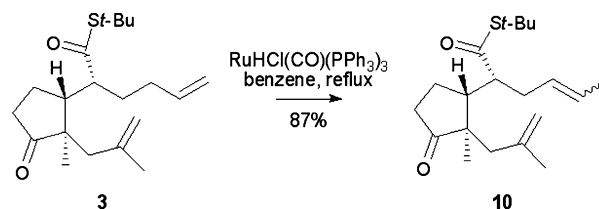
Methyl esters of both of the series, with methallyl or allyl substituents, **27–31**, were prepared from the respective thioesters by methanolysis using potassium methoxide in methanol (Scheme 5, Table 7). Under these conditions, the respective products were formed as mixtures of epimers, l,l (**27** and **30**) and u,l (**29** and **31**), in a ratio of ca. 1 : 1. The epimers were separated by flash chromatography. It is noteworthy that methanolysis of the very sterically congested thioester **18** gave a single epimer of the product, **28**.


**Scheme 3** The synthesis of diene **14**.

Scheme 4 The synthesis of diene **10**.

Thioester **17** and ester **31** were transformed into their respective derivatives **37**, **38**, **39**, and **40**, as indicated in Scheme 6. Two issues related to these transformations should be singled out for comment. Since the hydrolysis of benzoate **38** with KOH in MeOH was slow, the MeOK/MeOH system was used. In the ¹³C NMR spectrum of hydroxy ketone **39** (in CDCl₃) no carbonyl signal appeared, which might be indicative of the intramolecular
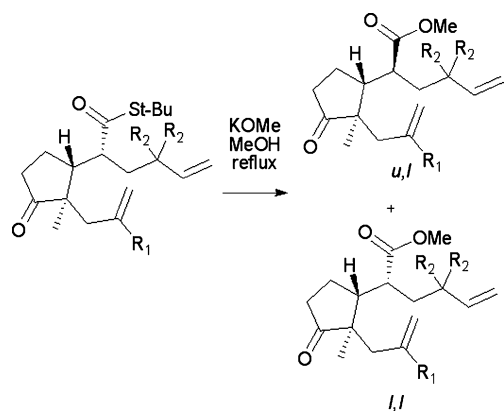
Scheme 5 The preparation of methyl esters **27–31** from their respective thioesters.
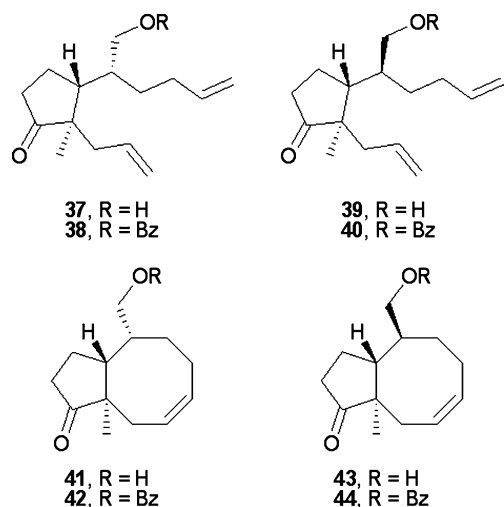
Scheme 6 Syntheses of alcohols **37**, **39** and benzoates **38**, **40**.

acetal formation; the respective IR spectrum (nujol) confirmed the presence of hydroxy- and keto- groups.

Conclusion

In conclusion, sterically congested 1,9-dienes related to *trans*-1-allyl-2-(pent-4-enyl)cyclopentane, when treated with Grubbs' ruthenium catalyst **7**, undergo either "direct" ring closing metathesis to afford the corresponding cyclooctene derivatives or a tandem double bond migration–metathesis reaction to form cycloheptene derivatives. The presence of a *S*-alkoxythiocarbonyl or alkoxycarbonyl group in position 2 and a *l*,*l* relative configuration have been found to be essential for the tandem process. In the bond migration–metathesis process, the formation of seven-membered ring derivatives appears to be favoured.

The Grubbs' metathesis catalyst and the double bond migration catalyst, RuClH(CO)(PPh$_3$)$_3$ (**9**), are compatible. The simultaneous use of these two catalysts facilitates the tandem bond migration–metathesis process. An application of the catalyst **9** alone in a unactivated double bond transpositioning of a preparative value is described.

A series of dienes for the metathesis study were synthesized, starting from 2-methylcyclopent-2-en-1-one, cyclopent-2-en-1-

one, or 2-methylcyclohept-2-en-1-one, the suitable *S*-*tert*-butyl alkenylthiocarboxylates and alkyl allyl carbonates, using tandem Mukaiyama–Michael addition and Tsuji alkylation reactions. A modified catalyst, consisting of palladium acetate and 1,4-(diphenylphosphine)butane (dppb), permitted the application of sterically demanding alkyl 2-methylprop-2-enyl carbonates in the alkylation step.

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