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Ring-closing metathesis, Kharasch addition and enol ester synthesis catalysed by a novel class of ruthenium(II) complexes

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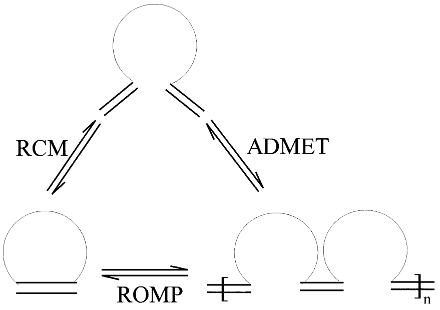
Abstract—Ruthenium Schiff base complexes **I**–**III** mediated the Kharasch addition of carbon tetrachloride across olefins with high yields which markedly depended on the catalyst and the substrate used. In addition, ring-closing metathesis of some representative diolefins was carried out. The best catalytic system **III** is able to form tri- and tetrasubstituted double bond products. Finally, dependent of the catalytic system and the reaction conditions used, these systems can catalyse the stereoselective formation of enol esters or enynes in excellent yields. © 2001 Elsevier Science Ltd. All rights reserved.

Since ruthenium has a $4d^75s^1$ electronic configuration, it has the widest range of oxidation states (from −2 in $Ru(CO)_4^{-2}$ to +8 in RuO_4) of all the elements and various coordination geometries in each electronic configuration, which represents a great potential for the exploitation in catalytic reactions. However, until the 1980s the useful methods were limited to a few reactions including proposals for oxidations with RuO_4, homogeneous hydrogenations for fine chemicals, hydroformylations and hydrogen transfer reactions. As the coordination chemistry of ruthenium complexes has progressed, characteristic features of ruthenium (e.g. high electron transferability, low redox potentials, stability of reactive metallic species, metallacycles, metal carbenes) have opened for a broad variety of catalytic transformations.[1] These include olefin metathesis, Kharasch addition reactions and enol ester synthesis. Olefin metathesis is a catalytic reaction in which alkenes are converted into new products via the rupture and reformation of C–C double bonds. Depending on the starting material (cyclic or acyclic alkenes) and the reaction parameters, ring-closing metathesis (RCM), acyclic diene metathesis (ADMET) or ring-opening metathesis polymerisation (ROMP) proceed (Scheme 1).[2]

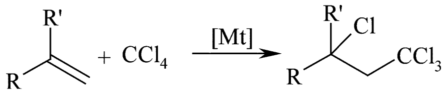
The Kharasch reaction consists of the addition of a polyhalogenated alkane across an olefin through a radical mechanism (Scheme 2).[3]

In the enol ester synthesis the ruthenium(II) complexes promote the electrophilic activation of alkynes to give Markovnikov or anti-Markovnikov (*E* and *Z*) addition reactions of carboxylic acids to the triple bond (Scheme 3).[4]

There exists an extensive chemistry of [(arene)-RuX_2PR_3] complexes and their activity in ring-closing metathesis, Kharasch addition reactions and enol ester synthesis.[5] In contrast, analogous half-sandwich Schiff base complexes are virtually unknown. Therefore, we investigated the activity of three new Schiff base-arene-ruthenium(II) complexes (Scheme 4) for the three above-mentioned reactions.



Scheme 1.



Scheme 2.

Keywords: ring-closing metathesis; Kharasch addition; enol ester synthesis; catalysis; ruthenium and compounds.

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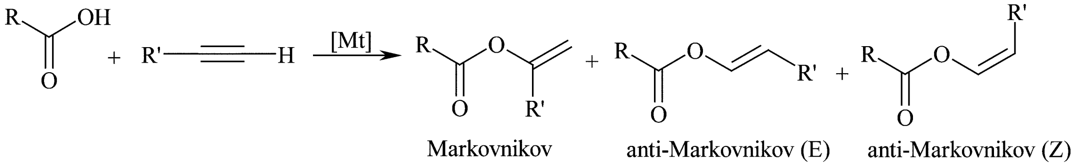
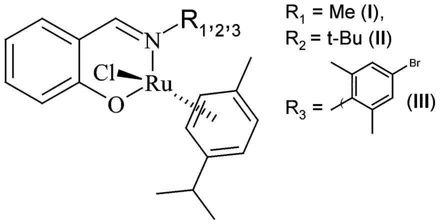


Scheme 3.

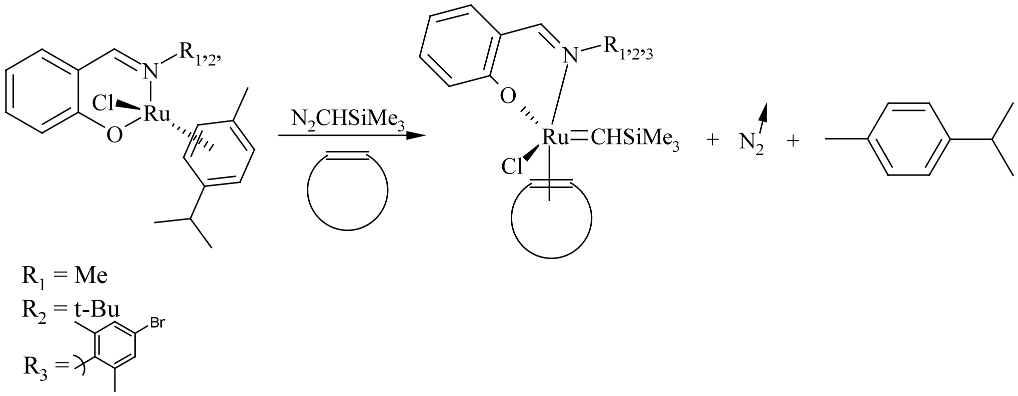


Scheme 4.

These systems were fully characterised by Raman, IR, ^{1}H, ^{13}C and elemental analysis.[6] To generate the metal carbene which is necessary in metathesis reactions, a catalytic amount of trimethylsilyldiazomethane (TMSD) was slowly added to the Ru-species. Studies by other teams dealing with metathesis reactions mediated by ruthenium arene complexes have shown that the release of the arene ligand is crucial and is responsible for the generation of the active catalyst.[7] Therefore, we suggest that the mechanism depicted in Scheme 5 is responsible for the formation of the catalytically active species in RCM reactions with **I**, **II** and **III**.

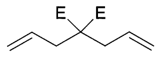
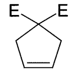
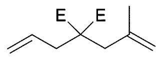
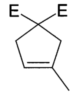
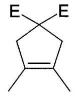
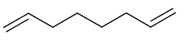
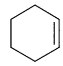
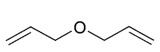
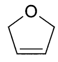
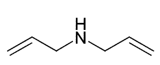
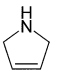
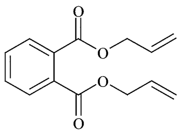
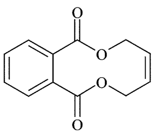
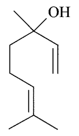
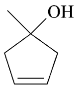
The ring-closing metathesis activities of complexes **I**, **II** and **III** are summarised in Table 1. Catalytic RCM of dienes diethyldiallylmalonate (entry 1), 1,7-octadieen (entry 4) and diallylether (entry 5) was performed quantitatively by all three systems. As can further be seen from the results in Table 1, the reactivity of the complexes is sufficiently high to allow the preparation of trisubstituted cycloalkenes at 70°C in moderate yields (entry 2). By using more harsh reaction conditions however (higher reaction temperatures and longer reaction times), the conversion increases dramatically. Under these forced conditions, the best catalytic system (**III**) reaches conversions of 71 and 23% for the tri- and tetrasubstituted malonatederivate, respectively (entries 2 and 3). Furthermore, also diallylphtalate (entry 7) and linalool (entry 8) are converted smoothly. With the best catalytic system **III** and when heating the reaction mixture for 17 h at 85°C conversions of 94 and 76%, respectively are reached. One important limitation for RCM reactions catalysed by these complexes, however, was encountered during this investigation. All attempts to convert diallylamine (entry 6) failed. Even when using the more harsh reaction conditions, no ring closing metathesis occurred.

The Kharasch addition reactions were performed using standard conditions. It appeared that the outcome of the reaction depended very much on the olefin and the catalytic system used (Table 2). Methylmethacrylate and styrene underwent a clean monoaddition of CCl_4 in the presence of the best catalytic complex **III**, and yielded as much as, respectively, 73 and 88% product after 17 h at 65°C. Performing the reactions with diethylallylmalonate led to a striking differentiation between the different catalytic complexes. Compounds **I** and **II** catalysed the reaction with a conversion round 40%, whereas **III** showed a conversion of 56%. Examination of data gathered in Table 2 also shows that with all three systems methacrylates are more smoothly converted than acrylates. For the best catalytic system **III** the reaction was also carried out at 85°C instead of 65°C (reaction time 17 h). In this case all substrates reached higher conversions. Styrene which is the best substrate for this type of catalysts, was nearly quantita-



Scheme 5.

Table 1. Ring-closing metathesis results of representative diolefins

				Yield, %[a]		
Entry	Substrate[b]	Product	Time (min.)	I	II	III
1			60[c]	100	100	100
2			60[c]	22	26	32
			1020[d]	46	53	71
3			60[c]	<5	<5	<5
			1020[d]	8	15	23
4			60[c]	100	100	100
5			60[c]	100	100	100
6			60[c]	<5	<5	<5
7			60[c]	48	55	60
			1020[d]	62	78	94
8			60[c]	16	21	28
			1020[d]	33	65	76

[a] Yield as determined with ^{1}H-NMR analysis and confirmed by GC using 1,3,5-mesitylene as internal standard. The formation of cycloisomers, oligomers or telomers was ruled out by GC analysis of the reaction mixture. The reaction products were unambiguously identified by comparison of the reaction products with the spectral data of authentic samples. Authentic samples were obtained by purification of the concentrated reaction mixtures by flash column chromatography using silica gel.

[b] E = COOEt.

[c] Reaction conditions: 70 °C; 5 mol% **I**, **II**, **III** in toluene; 2.2 equivalents TMSD.

[d] Reaction conditions: 85 °C; 5 mol% **I**, **II**, **III** in toluene; 2.2 equivalents TMSD.

tively transformed but also methylmethacrylate reached up to 84% conversion.

In Table 3 the results of the enol ester synthesis using systems **I**, **II** and **III** are summarised. When octadiyne is used as a substrate, the addition of both carboxylic acids result in the selective formation of (*E*)-alk-1-en-yl esters corresponding to a regio- and stereoselective anti-Markovnikov addition of the acid to the triple bond. The percentage of (*E*)-alk-1-en-yl ester is for all three catalytic systems and both acids more or less the same and varies in the range of 71–79%. The total yield, however, is very dependent of the type of catalyst and acid used. Again system **III** is the most active. Whereas with formic acid a total yield of 71% is obtained, up to 76% of total conversion is reached for the addition of acetic acid to octadiyne. To our knowledge, system **III** is one of the most active ruthenium catalysts reported so far for the selective formation of (*E*)-alk-1-en-yl esters out of alkadiynes and saturated carboxylic acids. Besides the formation of the (*E*)-alk-1-en-yl ester, also a small percentage of (*Z*)-alk-1-en-yl ester, Markovnikov addition products and disubstituted enol esters is obtained.

Table 2. Kharasch addition of carbon tetrachloride to representative olefins catalysed by ruthenium complexes **I**, **II**, **III**[a]

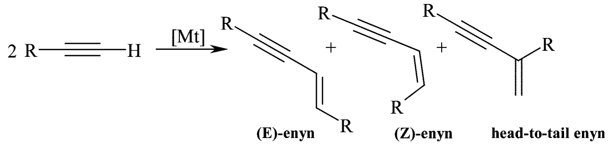
	I[b]	II[b]	III[b]	III[c]
Methylmethacrylate	62	66	73	84
Isobutylmethacrylate	24	26	34	52
Methylacrylate	18	22	26	33
Butylacrylate	9	12	12	18
Styrene	72	72	88	91
Acrylonitrile	<5	<5	<5	<5
Diethylallylmalonate	38	42	56	76

[a] Yields based on GLC using dodecane as internal standard.

[b] Reaction conditions. Prior to use, the reagents, the solvent (toluene) and the internal standard (dodecane) were dried using well established procedures, distilled and kept under nitrogen at −20°C. The catalyst (0.03 mmol) was dissolved in toluene (1 ml) and subsequently added through a septum to the solution of alkene (9 mmol), CCl_4 (13 mmol), dodecane (0.25 ml) in toluene (3 ml). The reaction mixture was heated at 65°C for 17 h.

[c] Idem as [b] but here the reaction mixture was heated at 85°C for 17 h.

It is known from literature that a limitation of ruthenium(II) complexes containing an electron-donating bidentate nitrogen ligand is the ability of these complexes to dimerise terminal alkynes into enynes (Scheme 6).[8,9]



Scheme 6.

When phenylacetylene is used as an alkyne source, the above-mentioned dimerization reaction becomes very important. With compound **II**, almost no nucleophilic addition of the carboxylic acid to the triple bond occurs and the (*E*)-enyne is formed with a selectivity of about 75% reaching a total yield of about 80%. Compounds **I** and **III** show a totally different behaviour. When using phenylacetylene, the outcome of the reaction depends on the carboxylic acid used. With formic acid, both systems form selectively the (*E*)-alk-1-en-yl ester. Performing the reaction with acetic acid leads to the stereoselective formation of the (*E*)-enyne. In this case, system **III** reaches an excellent total yield of 96% and a selectivity of 78% for the formation of the (*E*)-enyne.

In conclusion, the catalytic systems **I**, **II** and **III** are highly efficient multifunctional catalysts for promoting ring-closing metathesis and Kharasch addition reactions. Furthermore, dependent on the catalytic compound and the reaction conditions, they can catalyse the stereoselective formation of enol esters or enynes in very good yields.

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Table 3. Synthesis of enol esters from phenylacetylene, octadiyne and ruthenium catalysts **I**, **II** and **III**[a]

			Total yield (%)[b]	M.[c] (%)	anti-M. (*Z*)[c] (%)	anti-M. (*E*)[c] (%)	Head-to-tail enyn[c] (%)	(*Z*)-Enyn[c] (%)	(*E*)-Enyn[c] (%)
I	ph.ac.	f. ac.	16	19	17	64	–	–	4
		ac. ac.	44	5	3	10	2	9	71
II	ph.ac.	f. ac.	78	7	2	9	–	6	76
		ac. ac.	80	7	2	7	4	8	74
III	ph.ac.	f. ac.	74	12	/	79	–	4	5
		ac. ac.	96	3	2	9	3	5	78
							% Disubstituted enol ester		
I	octad.	f. ac.	19	12	10	72	6		
		ac. ac.	49	14	6	75	5		
II	octad.	f. ac.	25	12	9	71	8		
		ac. ac.	64	14	9	73	4		
III	octad.	f. ac.	71	11	6	76	7		
		ac. ac.	76	13	5	79	3		

[a] The reactions were carried out by using 4.4 mmol of carboxylic acid, 4.4 mmol of alkyne and 0.04 mmol of catalyst in 3 ml toluene at 100°C for 4 h under an inert atmosphere.

[b] The total yield was determined with Raman spectroscopy by following the diminishing intensity of the $\nu_{C\equiv C}$ of phenylacetylene (ph.ac.) and octadiyne (octad.) and using a calibration curve (f. ac. = formic acid, ac. ac. = acetic acid). Conformation was obtained by GC–MS.

[c] The selectivities were determined by GC–MS making use of the different fragmentations of the isomers. GC–MS measurements excluded also the formation of other products than those reported here. (% M = percentage Markovnikov addition product, % anti-M = percentage anti-Markovnikov addition product)

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