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Kharasch addition and vinylation reactions mediated by ruthenium(II) complexes bearing Schiff base ligands

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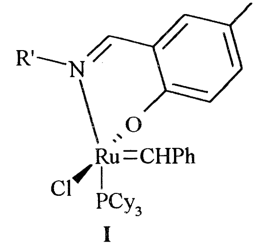
Ruthenium Schiff base complexes **I.a-f** mediated the Kharasch addition of carbon tetrachloride across olefins with high yields which markedly depended on the catalyst and the substrate used. Furthermore, 1,6-dienes undergo a highly stereoselective addition–cyclization process with these systems to give mixtures of *cis*- and *trans*-3-chloromethyl-4-(2,2,2-trichloroethyl)cyclopentanes in excellent yields. Finally, the catalytic performance of these systems in the vinylation reaction was checked. Dependent on the catalytic system and the reaction conditions used, enol esters or enynes can be obtained in high yields with moderate selectivities.

KEY WORDS: Kharasch addition; ATRA; vinylation; Ru complexes; Schiff base; homogeneous catalysis.

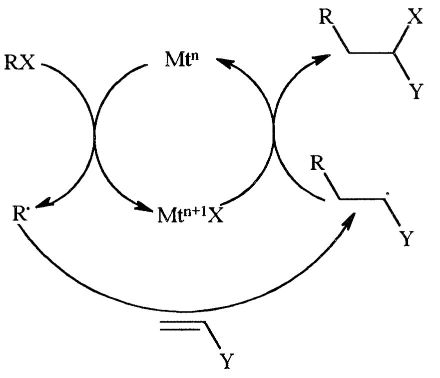
Customary, organometallic catalytic complexes are synthesized and optimized to perform a single reaction [1]. However, demands from industry for cost-efficient and environmentally benign synthetic processes have stimulated the research for catalytic organometallic compounds that can mediate multiple mechanistically distinct steps in the reaction sequence of a synthetic pathway [2]. Previous studies from our group pointed out that ruthenium(II) complexes bearing Schiff base ligands were capable of performing various organic reactions in good to excellent yields [3]. These promising results prompted us to further investigate the capacities of these systems. Now we report on the activity of catalytic systems **I.a-f** (figure 1) in Kharasch and vinylation reactions. These systems were fully characterized by Raman, IR, ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR and elemental analysis [4].

The Kharasch reaction catalyzed by transition metals has attracted much attention since the early 1970s [5]. Furthermore, the extension of the Kharasch addition to atom transfer radical polymerization (ATRP) has recently revitalized the research in this area as well [6]. This reaction consists of the addition of a polyhalogenated alkane across an olefin through a radical mechanism (Scheme 1) [7]. This carbon–carbon and carbon–halogen bond-formation is now typically catalyzed by transition metal complexes.



a. R = H, R' = Me
b. R = NO$_2$, R' = Me
c. R = H, R' = 2,6-Me-4-BrC$_6$H$_2$
d. R = NO$_2$, R' = 2,6-Me-4-BrC$_6$H$_2$
e. R = H, R' = 2,6-iPrC$_6$H$_3$
f. R = NO$_2$, R' = 2,6-iPrC$_6$H$_3$

Figure 1.



Scheme 1.

In the vinylation or 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 2) [8].

However, it is known from the literature that a limitation of ruthenium(II) complexes containing an electron-donating bidentate nitrogen ligand is the ability of these complexes to dimerize terminal alkynes into enynes (Scheme 3) [9].

In a first set of experiments we tested the performance of catalytic systems **I.a-f** in Kharasch reactions. Table 1

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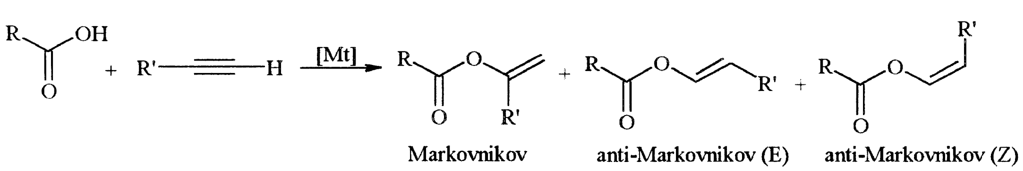
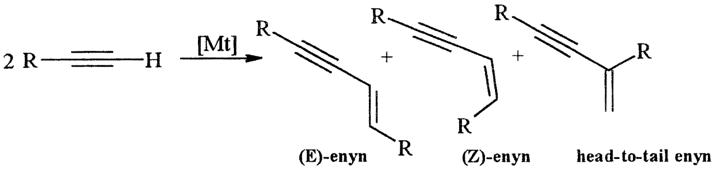


Scheme 2.



Scheme 3.

summarizes representative Kharasch processes mediated effectively by systems **I.a-f** under standard conditions. It appeared that the outcome of the reaction depended very much on the olefin and the catalytic system used. For all substrates the activity decreases in the order of **I.d** > **I.c** > **I.f** > **I.e** > **I.b** > **I.a**. For example, system **I.d** converts styrene and diethylallylmalonate in 87 and 86% yield, respectively, whereas the worst-performing catalyst **I.a** only reaches 58 and 66% conversion, respectively, for both substrates.

Styrene and diethylallylmalonate are clearly the two substrates that allow the highest turnover, irrespective of the catalytic system used. Comparing the yields for methylacrylate (MA) and butylacrylate (BA) on one hand, and methylmethacrylate (MMA) and isobutylmethacrylate (IBMA) on the other, reveals that the conversion decreases when the substrate becomes too bulky, as for all catalysts. For example, the best-performing system **I.d** yields halogenated MA and MMA in respectively 20 and 25% conversion, whereas their more bulky counterparts BA and IBMA are converted in a mere 16 and 18% yield. Another striking feature that can be revealed from the results gathered in table 1 is the spectacular increase of conversion with temperature for the best-performing system **I.d**. For example, when the reaction mixture is stirred at 85 °C for 17 h instead of 65 °C for 17 h, nearly quantitative conversions for styrene and diethylallylmalonate are obtained. Further examination of data gathered in table 1 leads to the conclusion that the activity of the catalyst increases when the Schiff base is substituted with an electron-withdrawing functionality (*e.g.*, a nitro group). Moreover, when comparing the catalytic performance of **I.a** or **I.b** with the other systems, it is clear that a certain degree of bulkiness in the Schiff base is needed to obtain good conversions. However, the influence is rather subtle, as can be seen from the comparison between the activities of systems **I.c** with **I.e** or **I.d** with **I.f**. Indeed, comparing these series of catalysts leads to the conclusion that the Schiff base ligands should not be too bulky, because then a decreased catalytic performance is observed. For example, whereas **I.c** reaches 82% conversion for styrene, system **I.e** containing the isopropyl substituted aromatic Schiff base converts the same substrate in only 68% yield.

Table 1
Kharasch addition of carbon tetrachloride to representative olefins catalyzed by ruthenium complexes **I.a-f**.[a]

	I.a[b]	**I.b**[b]	**I.c**[b]	**I.d**[b]	**I.e**[b]	**I.f**[b]	**I.d**[c]
Methylmethacrylate	7	9	18	25	11	15	51
Isobutylmethacrylate	5	6	12	18	6	9	30
Methylacrylate	6	6	15	20	7	10	44
Butylacrylate	<5	7	11	16	8	11	26
Styrene	58	63	82	87	68	76	98
Acrylonitrile	<5	<5	8	13	<5	8	21
Diethylallylmalonate	66	69	78	86	71	75	94

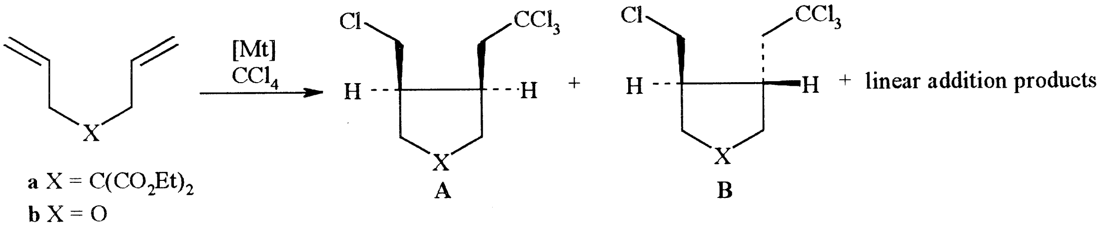
[a] Yields based on GLC using dodecane as internal standard.

[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 a 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] As [b] but here the reaction mixture was heated at 85 °C for 17 h.

Concerning the Kharasch addition reaction, we also studied the ruthenium(II) catalyzed addition of carbon tetrachloride to two 1,ω-dienes, namely diethyldiallylmalonate and diallylether. The possible addition reaction products are depicted in Scheme 4 and the yield (%) and diastereoselectivities of these experiments are summarized in table 2.

First, note that in all cases no linear addition products and 6-membered rings were observed. So only the 5-membered cyclic addition products have to be taken into consideration. For 1,ω-dienes, the selective formation of 5-membered rings *via* a 5-exo-trig cyclization instead of 6-membered rings *via* a 6-endo-trig cyclization (Scheme 5) is well known and various explanations for the observed regiospecificity have been advanced, including entropic [11], steric [12] and stereoelectronic [13] factors.



Scheme 4.

As can be seen from the results gathered in table 2, the regiospecific radical addition of the two 1,ω-dienes is also highly stereoselective for the formation of the *cis*-isomers (compounds **A.a** and **A.b** in Scheme 3). For example, system **I.d** produces the ring-closed products **A.a** and **A.b** in respectively 89 and 79% yield with selectivities for the *cis* isomers of respectively 89 (*cis*:*trans* ratio = 8.4:1) and 81% (*cis*:*trans* ratio = 4.2:1). All the conclusions concerning the steric bulk of the salicylaldimine ligands and electronic influence of the Schiff base substituents that were made for the vinylic substrates are also valid for the 1,ω-diene substrates. Indeed, here again **I.d** and **I.a** are respectively the highest and the lowest performing systems. To the best of our knowledge, catalyst **I.d** is the best ruthenium system reported so far that succeeds in producing ring-closed Kharasch addition products from 1,ω-dienes with excellent diastereoselectivities in such good yields.

Table 2
Diastereoselective Kharasch addition of carbon tetrachloride to representative olefins catalyzed by ruthenium complexes **I.a-f**.

	Diethyldiallylmalonate/diallylether					
	I.a[b]	**I.b**[b]	**I.c**[b]	**I.d**[b]	**I.e**[b]	**I.f**[b]
Yield (%)[a]	68/54	72/55	85/72	89/79	74/61	80/67
Product *cis*:*trans* ratio[c]	2.2/1.1	2.8/1.3	5.8/2.9	8.4/4.2	3.0/1.8	3.6/2.4

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

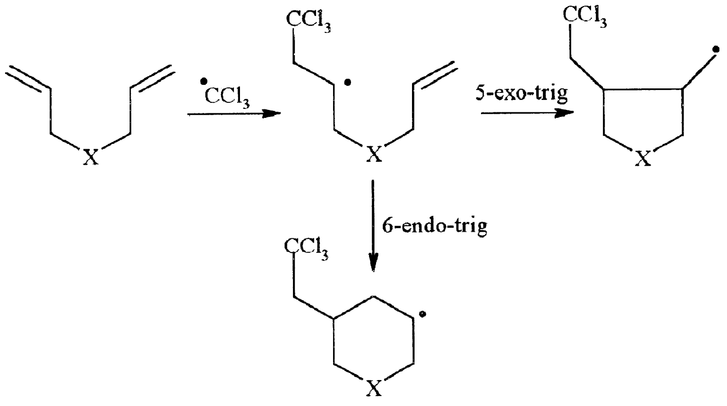
[b] Reaction conditions as in table 1. The reaction mixture was heated at 65 °C for 17 h.

[c] The presence of cyclic reaction products from our radical addition–cyclization reactions was proven on the basis of NMR data. The ^{13}C-APT-NMR spectrum of the mixture of isomers allowed identification of the CH_2Cl, CH_2CCl_3 and cyclic CH carbon atoms. The presence of a *cis* and a *trans* stereochemistry of the cyclic reaction products was proven by the presence of two CH_2Cl and two CH_2CCl_3 carbon atom peaks in the ^{13}C-NMR spectrum. Because of the so-called γ-effect whereby a carbon atom *cis* to another carbon at the γ position suffers extra shielding as compared with a *trans* carbon [10], the chemical shifts for CH_2Cl in **A.a** and **B.a** are 44.6 and 46.0 ppm respectively and 54.31 and 59.2 ppm for CH_2CCl_3 (when using tetramethylsilane as internal standard). The *cis*:*trans* ratio was calculated by integration of the ^{1}H-NMR spectrum of the reaction mixture. The reaction products **A.a-b** and **B.a-b** 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. Selected ^{1}H-NMR data for *cis*- and *trans*-diethyl-3-chloromethyl-4-(2,2,2-trichloroethyl)-cyclopentane-1,1-dicarboxylate (respectively **A.a** and **B.a**): For **A.a** δ 2.98 (2 × m, A_2BX_2 multiplet, 2H, CH_2CCl_3), 3.64 (2 × m, A_2BX_2 multiplet, 2 H CH_2Cl); for **B.a** δ 3.05 (2 × d, A_2B doublet, 2 H, CH_2CCl_3), 3.70 (2 × d, A_2B doublet, 2 H, CH_2Cl). Selected ^{1}H-NMR data for *cis*- and *trans*-3-chloromethyl-4-(2,2,2-trichloroethyl)tetrahydrofuran (respectively **A.b** and **B.b**): for **A.b** δ 3.90 (2 × m, A_2BX_2 multiplet, 2H, CH_2CCl_3), 4.93 (2 × m, A_2BX_2 multiplet, 2 H, CH_2Cl); for **B.b** δ 3.05 (2 × d, A_2B doublet, 2 H, CH_2CCl_3), 4.99 (2 × d, A_2B doublet, 2 H, CH_2Cl).

The observed variations in diastereoselectivity of cyclization indicate that the complex must be intimately involved in the cyclization mechanism. However, the exact role of the catalytic complex remains unknown because any type of close association of the complex, either with the intermediate radical or with the olefinic bond undergoing attack, would be expected to alter the steric and stereoelectronic factors known to determine the diastereoselectivity of cyclization of 1,5-disubstituted-5-hexenyl radicals.

In a second set of experiments, we conducted vinylation reactions using catalytic systems **I.a-d**. The results of these tests are depicted in table 3. When octadiyn 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 similar for all four catalytic systems and both acids and varies in the range of 67–75%. The total yield, however, is very dependent on the type of catalyst and acid used. Now system **I.a** is the most active. Whereas with formic acid and acetic acid a total yield of respectively <5% and 21% is obtained, with the worst-performing system **I.d**, up to 40 and 45% of total conversion is reached with **I.a**. 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 are obtained.

When phenylacetylene is used as the alkyne source, the dimerization reaction depicted in Scheme 3 becomes very important. Indeed, with all catalytic systems both the nucleophilic addition of the carboxylic acid to the triple bond forming the (*E*) anti-Markovnikov adduct and the alkyne dimerization reaction producing the (*E*)-enyn must be taken into consideration. For example, when using acetic acid, the best-performing system **I.a** produces (besides a modest yield of the Markovnikov addition compound) the (*E*)-enyn and the (*E*)-anti-Markovnikov addition product with a selectivity of respectively 42 and 29% yield reaching a total yield of 98%. Concerning the selectivities of the formed reaction



Scheme 5.

Table 3
Synthesis of enol esters from phenylacetylene, octadiyn and ruthenium catalysts **I.a-f**.[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.a	ph.ac.	f. ac.	87	9	5	34	–	4	48
		ac. ac.	98	14	8	29	2	5	42
I.b	ph.ac.	f. ac.	81	11	4	39	–	2	44
		ac. ac.	88	10	7	36	4	5	38
I.c	ph.ac.	f. ac.	76	15	6	31	2	4	42
		ac. ac.	95	18	9	27	3	6	37
I.d	ph.ac.	f. ac.	67	12	8	30	2	7	41
		ac. ac.	75	16	11	29	–	8	36
								% disubstituted enol ester	
I.a	octad.	f. ac.	40	14	11	67		8	
		ac. ac.	45	15	8	72		5	
I.b	octad.	f. ac.	31	13	12	69		6	
		ac. ac.	36	11	10	70		9	
I.c	octad.	f. ac.	12	16	9	71		4	
		ac. ac.	40	13	7	75		5	
I.d	octad.	f. ac.	<5	11	9	73		7	
		ac. ac.	21	–	–	–		–	

[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 octadiyn (octad.) and using a calibration curve. (f. ac. = formic acid, ac. ac. = acetic acid).

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

products, the same tendency is observed for all the other catalytic systems. Furthermore, with phenylacetylene as the alkyne reaction partner, all the catalytic complexes were devoid of any significant activity for the formation of the head-to-tail enyn. Moreover, also the (*Z*)-enyn and the (*Z*)-anti-Markovnikov products were observed only as traces.

In conclusion, the catalytic systems **A.a-f** are highly efficient catalysts for promoting Kharasch addition reactions of CCl_4 to terminal alkenes. 1,6-Dienes undergo an excellent stereoselective addition–cyclization process in very high yields. Furthermore, we also checked the activity of these complexes in vinylation reactions. Dependent on the reaction conditions, they can catalyze the formation of enol esters or enynes in high yields with moderate stereoselectivities.

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