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Atom-Transfer Radical Addition (ATRA) and Cyclization (ATRC) Reactions Catalyzed by a Mixture of [RuCl$_2$Cp*(PPh$_3$)] and Magnesium

Katrin Thommes,[a] Burçak Içli,[b] Rosario Scopelliti,[a] and Kay Severin*[a]

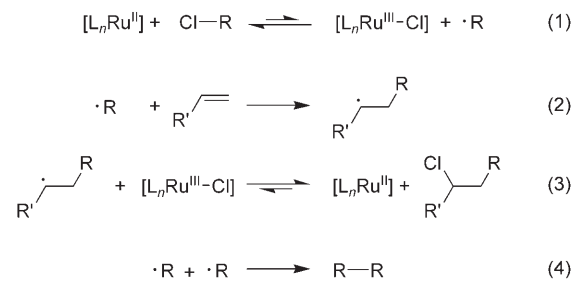
Abstract: A new catalytic procedure for atom-transfer radical addition (ATRA) and cyclization (ATRC) reactions is described. The combination of the ruthenium(III) complex [RuCl$_2$Cp*(PPh$_3$)] (Cp*: pentamethylcyclopentadienyl) with magnesium allows these reactions to be performed under mild conditions with high efficiency. In most cases, the catalyst concentrations required are significantly lower than those used in previously reported procedures. It is suggested that magnesium acts as a reducing agent that generates and regenerates the catalytically active ruthenium(II) species. The precatalyst [RuCl$_2$Cp*(PPh$_3$)] has been analyzed by X-ray crystallography.

Keywords: catalysis · cyclization · magnesium · radical reactions · ruthenium

Introduction

In 1945, Kharasch and co-workers reported that halocarbons, such as CCl_4, could be added to olefins through a radical chain process.[1] Three decades later, the scope of the reaction was expanded following the discovery that the ruthenium(II) complex [RuCl$_2$(PPh$_3$)$_3$] (**1**) was able to act as an efficient catalyst for this reaction.[2] The main advantage of the ruthenium-catalyzed version of the reaction is that side reactions are reduced. For the next 25 years, complex **1** was among the most frequently used catalyst for intra- and intermolecular atom-transfer radical addition (ATRA) reactions of halogenated compounds to olefins and interesting applications in organic synthesis have been developed.[3] Over the last seven years, however, several ruthenium catalysts with improved catalytic performances have been reported.[4,5] These catalysts allow ATRA reactions to be carried out at ambient temperatures with turnover frequencies (TOFs) of up to 1500 h^{-1}. Despite this high activity, the new catalysts still have a severe drawback: they display low catalyst stability. Consequently, only low turnover numbers (TONs) are achieved; this is particularly evident for addition reactions with substrates that show a low intrinsic reactivity, such as $CHCl_3$ or 1-decene. In these cases, the maximum TONs generally do not exceed 300.[6]

It is generally assumed that ruthenium-catalyzed ATRA reactions proceed in three steps.[4] These reactions are depicted in Equations (1–4) for the addition of a chloro compound (Cl−R) to a terminal olefin (R′CH=CH$_2$).



First, a [Ru^{II}L$_n$] complex abstracts a chloro atom from Cl−R to give a [Ru^{III}ClL$_n$] complex and an R$^•$ radical [Eq. (1)]. The radical adds to the olefin [Eq. (2)], which then reacts with the [Ru^{III}ClL$_n$] complex to give the 1:1 addition product and also the regenerated [Ru^{II}L$_n$] catalyst [Eq. (3)]. For ATRA reactions with CCl_4, it had been reported that an increased CCl_4 concentration leads to faster catalyst decomposition[5j] and that the reaction of a Ru^{II} catalyst with CCl_4 in the absence of olefin produces C_2Cl_6.[5b,7] These observations suggest that the combination of two $^•CCl_3$ radicals occurs as

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side reaction. Termination reactions between two R$^{\bullet}$ radicals are also likely to occur for other ATRA reactions [Eq. (4)], which would lead to an accumulation of [$Ru^{III}ClL_n$] complexes and to a decrease in catalytic rate. If termination reactions are a limiting factor, then it should be possible to increase the lifetime of the catalyst by the addition of a reagent that could regenerate the [$Ru^{II}L_n$] complex. In a recent communication we have shown that this is indeed the case, when azobis(isobutyronitrile) (AIBN, 5 mol%) was added to ATRA reactions, significantly improved TONs were obtained.[8] The role of AIBN is to provide a source of radicals that can regenerate the [$Ru^{II}L_n$] catalyst through the abstraction of a chloro atom from [$Ru^{III}ClL_n$]. An advantage of this methodology, aside from the low catalyst loadings, is the fact that an air-stable and easy to handle Ru^{III} catalyst, such as **1,** can be used as the catalyst precursor. A related strategy has been employed for copper-catalyzed atom-transfer radical polymerization (ATRP) reactions, in which AIBN was used in combination with a stable Cu^{II} precatalyst to generate and regenerate the active Cu^{I} complex.[9]

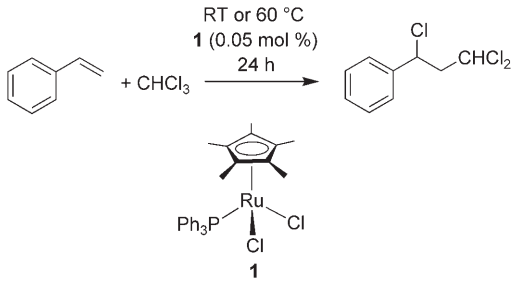
Despite the advantages outlined above, the use of AIBN also has some drawbacks. AIBN and its decomposition products increase the number of compounds (catalyst, excess Cl–R, and side products) that need to be removed during purification of the product. Furthermore, the reactions have to be heated because AIBN is not an efficient radical source at ambient temperatures. Most importantly, AIBN is able to initiate polymerization of the olefinic substrate, which may result in an increased formation of oligomers instead of the desired 1:1 addition product. The latter process is particularly problematic for highly reactive olefins, such as methacrylates.

To circumvent the problems associated with AIBN, we have investigated the possibility of employing alternative reducing agents for the regeneration of Ru^{II} catalysts. The ideal reagent should be commercially available, cheap, nontoxic, easy to handle, and easy to separate. Herein, we show that magnesium, which fulfills all the criteria mentioned above, is an excellent additive for Ru-catalyzed ATRA reactions. In combination with **1** as the catalyst precursor, it is possible to perform intra- and intermolecular ATRA reactions at room temperature with exceptional efficiency.

Results and Discussion

In the first set of experiments, we investigated the effect of various additives for the ATRA reaction of chloroform to styrene when complex **1** was used as the catalyst. The addition of $CHCl_3$ to styrene was chosen as the screening reaction because it is a simple, but relatively "difficult" ATRA reaction. Any system that gives good results for this reaction should also be of interest for other synthetically more interesting reactions. In the first attempt, we investigated the effect of employing zinc as an additive. Metallic Zn is well known for its ability to reduce [$Ru^{III}Cp^*$] (Cp*: pentamethylcyclopentadienyl) complexes to the corresponding [$Ru^{II}Cp^*$] complexes.[10] However, the ATRA reaction with complex **1** (0.05 mol%) and Zn (100 mg, 1.1 equiv with respect to styrene) gave only trace amounts of the product after 24 h (Table 1, entry 1). Significantly higher yields were

Table 1. ATRA reaction of $CHCl_3$ to styrene catalyzed by complex **1** in the presence of various additives.[a]



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Entry	Additive[b]	T [°C]	Conv.[c] [%]	Yield[d] [%]
1	1.1 equiv Zn	RT	8	3
2	3.0 equiv Mg	RT	41	39
3	3.0 equiv Mg[e]	RT	58	55
4	0.3 equiv Mg[e]	RT	30	28
5	3.0 equiv Mg[e], D_2O[f]	RT	91	86
6	3.0 equiv Mg[e], D_2O[g]	RT	44	33
7	3.0 equiv Mg[e], Et_2O[h]	RT	55	50
8	3.0 equiv Mg[e], THF[h]	RT	81	36
9	5 mol% AIBN	60	100	80

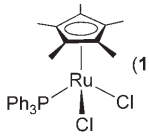
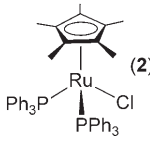
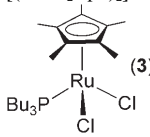
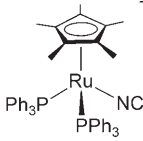
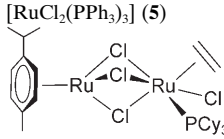
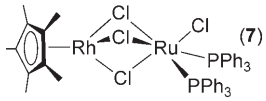
[a] The reactions were performed with $CHCl_3$ as the solvent (total volume = 1000 μL, [olefin] = 1.38 M). [b] Equivalents with respect to styrene. [c] The conversion (conv.) is based on the consumption of the olefin. [d] The yield is based on the formation of the product as determined by ^{1}H NMR spectroscopy after 24 h by using the internal standard 1,4-bis(trifluoromethyl)benzene (270 mM). [e] The magnesium powder was agitated by means of a stirring bar under an atmosphere of dry nitrogen for 10 d before use. [f] $CHCl_3$ saturated with D_2O was used as the solvent. [g] D_2O (6 μL) was added directly to the reaction mixture. [h] THF (50 μL) or Et_2O (50 μL) were added to the reaction mixture.

observed when Mg powder (100 mg, 3.0 equiv with respect to styrene) was used instead of Zn: 39% of the desired 1:1 addition product was obtained after 24 h (Table 1, entry 2). When the surface of the Mg powder was activated prior to the reaction by agitation with a magnetic stirring bar,[11] an improved yield of 55% was obtained (Table 1, entry 3). However, reducing the amount of Mg from 100 to 10 mg (0.3 equiv) resulted in a lower yield (Table 1, entry 4). For some Ru-catalyzed ATRA reactions, we observed that a small amount of water can be beneficial.[5b,e] Therefore, we examined the reaction with activated Mg (100 mg) by using chloroform saturated with D_2O as the solvent. The presence of water did indeed result in an improved catalytic reaction and gave a final yield of 86% after 24 h (Table 1, entry 5). A larger amount of water was detrimental to the yield of the reaction, as shown by the results of the reaction in which D_2O (6 μL, 0.6 vol%) was added directly to the reaction mixture (Table 1, entry 6). Small amounts of diethyl ether as a polar co-solvent did not result in rate enhance-

ments (Table 1, entry 7) and the use of THF as a co-solvent led to the formation of significant amounts of side products and gave lower yields (Table 1, entry 8). It should be noted that the reaction performed in chloroform saturated with D_2O gave a yield of 86% at room temperature (Table 1, entry 5), which is even better than that achieved with AIBN at 60°C (Table 1, entry 9). Furthermore, the Mg co-catalyzed reaction gave less side products than the reaction that contained AIBN. The fact that complex **1** and Mg are both required for efficient conversion was shown by performing control reactions that contained either precatalyst **1** or the Mg co-catalyst, neither of which gave significant amounts of product (<2%).

Next, we investigated the catalytic activity of different Ru complexes by using the "optimal" conditions described above ($CHCl_3$ saturated with D_2O). The olefin/Ru ratio was again 2000:1 and the reactions were performed at room temperature. The Ru^{II} complex $[RuClCp^*(PPh_3)_2]$ (**2**) gave slightly lower yields than the parent Ru^{III} complex **1** (Table 2, entries 1 and 2). The latter can be prepared in situ by mixing commercially available $[(RuCl_2Cp^*)_2]$ with PPh_3 (2 equiv) without any loss of catalytic performance (Table 2, entry 3). Exchanging PPh_3 for $P(n\text{Bu})_3$ (Table 2, entries 4 and 5), PCy_3 (Cy: cyclohexyl), or $P(p\text{-}C_6H_4Cl)_3$ resulted in lower yields (Table 2, entries 4–7). Cationic Ru^{II} complex **4** has been described as one of the best catalysts for the addition of $CHCl_3$ to styrene,[6] but its performance (Table 2, entry 8) was found to be inferior to that of complex **1** (Table 2, entry 1). The "classical" ATRA reaction catalyst $[RuCl_2(PPh_3)_3]$ (**5**) and the bimetallic catalysts [(cymene)Ru-(μ-Cl)$_3$RuCl(C_2H_4)(PCy_3)] (**6**) and [Cp*Rh(μ-Cl)$_3$RuCl-(PPh_3)$_2$] (**7**), which were recently reported by our laboratory,[5b,e] gave only low conversions and yields under the present reaction conditions (Table 2, entries 9–11).

Table 2. ATRA reaction of $CHCl_3$ to styrene catalyzed by various Ru complexes in the presence of Mg.[a]

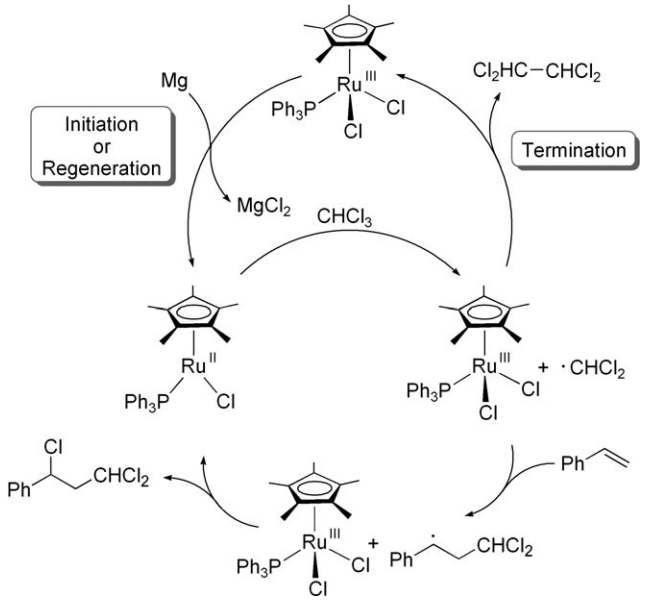
Entry	Ru complex	Conv.[b] [%]	Yield[c] [%]
1	 (**1**)	91	86
2	 (**2**)	89	81
3	$[(RuCl_2Cp^*)_2]$+2 PPh_3	91	84
4	 (**3**)	43	31
5	$[(RuCl_2Cp^*)_2]$+2 PBu_3	44	32
6	$[(RuCl_2Cp^*)_2]$+2 PCy_3	2	<2
7	$[(RuCl_2Cp^*)_2]$+2 $P(p\text{-}C_6H_4Cl)_3$	72	64
8	 (**4**)	65	56
9	$[RuCl_2(PPh_3)_3]$ (**5**)	4	<2
10	 (**6**)	8	<2
11	 (**7**)	7	<2

[a] The reactions were performed at room temperature in the presence of activated Mg powder (100 mg) in $CHCl_3$ saturated with D_2O as the solvent (total volume = 1000 μL, [olefin] = 1.38 M). [b] The conversion is based on the consumption of the olefin. [c] The yield is based on the formation of the product as determined by ^1H NMR spectroscopy after 24 h by using the internal standard 1,4-bis(trifluoromethyl)benzene (270 mM).

The proposed catalytic cycle for the addition of $CHCl_3$ to styrene when catalyzed by complex **1** and Mg is shown in Scheme 1. The reaction is initiated with the reduction of **1** by Mg to give the 16 electron complex $[RuClCp^*(PPh_3)]$. The latter abstracts a chloro atom from $CHCl_3$ to generate a $^{\bullet}CHCl_2$ radical, which adds to the olefin. The final addition product is then formed after the newly formed radical reacts with $[RuCl_2Cp^*(PPh_3)]$. Termination reactions, such as the homocoupling of two $^{\bullet}CHCl_2$ radicals, would normally result in an irreversible build up of the Ru^{III} complex $[RuCl_2Cp^*-(PPh_3)]$, but in the presence of Mg regeneration of the catalytically active Ru^{II} species is possible. The role of water within this catalytic cycle is not clear at present. It is conceivable, however, that water facilitates the heterogeneous reduction of complex **1** by Mg.

Although complex **1** has been known for many years,[10c] its solid state structure had not been determined. Therefore, we investigated single crystals of complex **1** by using X-ray crystallography. The complex shows the expected "piano stool" geometry (Figure 1). With values of 2.4042(5) and 2.3775(5) Å, respectively, the Ru–Cl bonds of **1** are shorter than those found for the related Ru^{II} complex $[RuClCp^*-(PPh_3)_2]$ (**2**) (2.4575(5) Å).[12] The Ru–P bond of **1**, on the other hand, is slightly longer than that observed for **2** (**1**: 2.3505(5) Å; **2**: 2.3364(6) and 2.3449(5) Å).

To test the scope of our new procedure by using complex **1** and Mg, we investigated a number of intra- and intermolecular ATRA reactions. Table 3 summarizes the results obtained for the addition of CCl_4 and $CHCl_3$. CCl_4 addition to aromatic or aliphatic olefins can be performed at room temperature with the Ru catalyst (0.02 mol%). After two to three days, the monoadducts were obtained from very clean reactions in good yields (Table 3, entries 1–4). A higher catalyst loading (0.05 mol%) allows the reaction times to be reduced to 24 h, as demonstrated for the disubstituted olefin α-methylstyrene (Table 3, entry 5). For these substrates, the previously reported procedure involving complex **1** and AIBN at 60°C also gave very good results.[8] A clear advantage of the new Mg-based method is observed for reactive olefins, such as methyl methacrylate, which have a high ten-



Scheme 1. Proposed catalytic cycle for the ATRA reaction of $CHCl_3$ to styrene catalyzed by complex **1** in the presence of Mg.

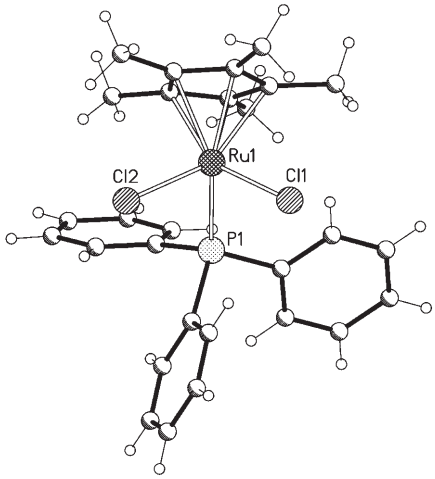


Figure 1. Graphic representation of the molecular structure of complex **1** in the crystal. The co-crystallized solvent molecules (1.5 C_6H_6) are not shown for clarity. Selected bond lengths (Å) and angles (°): Ru1−Cl1 = 2.4042(5), Ru1−Cl2 = 2.3775(5), Ru1−P1 = 2.3505(5); P1-Ru1-Cl2 = 86.516(19), P1-Ru1-Cl1 = 91.156(18), Cl2-Ru1-Cl1 = 101.332(18).

dency to polymerize. By using a substrate/catalyst ratio of 10000:1, we were able to obtain the CCl_4 adduct in a yield of 86% after only 24 h (Table 3, entry 6). This result corresponds to a TON of 8600, which is, to best of our knowledge, the highest value ever reported for this reaction.[13] Overall, one should note that despite the use of activated substrates, such as CCl_4 and *p*-chlorostyrene, the ATRA reactions are not affected by Mg-based organometallic chemistry.

Table 3. ATRA reaction of CCl_4 and $CHCl_3$ to olefins catalyzed by complex **1** in the presence of Mg.[a]

Entry	Olefin	R−Cl	[Ru]/[Olefin]	*t* [h]	Conv.[b] [%]	Yield[c] [%]
1	styrene	CCl_4	1:5000	72	100	97
2	*p*-chlorostyrene	CCl_4	1:5000	48	100	95
3	1-decene	CCl_4	1:5000	72	86	81
4	α-methylstyrene	CCl_4	1:5000	72	98	93
5	α-methylstyrene	CCl_4	1:2000	24	100	96
6	methyl methacrylate	CCl_4	1:10000	24	100	86
7	styrene	$CHCl_3$	1:2000	48	100	92
8	*p*-chlorostyrene	$CHCl_3$	1:2000	48	100	89
9	α-methylstyrene	$CHCl_3$	1:1000	72	43	26
10	methyl methacrylate	$CHCl_3$	1:500	72	94	48
11	1-decene	$CHCl_3$	1:500	72	23	21

[a] The reactions were performed at room temperature in the presence of activated Mg powder (100 mg) in toluene saturated with D_2O (entries 1–6) or in $CHCl_3$ saturated with D_2O (entries 7–11) as the solvent (total volume = 1000 μL, [olefin] = 1.38 M). [b] The conversion is based on the consumption of the olefin. [c] The yield is based on the formation of the product as determined by ^1H NMR spectroscopy by using the internal standard 1,4-bis(trifluoromethyl)benzene (270 mM).

Addition reactions that involve the significantly less active species $CHCl_3$, as opposed to CCl_4, are also possible at room temperature. Exceptionally high TONs of ≈1800 were obtained for the aromatic olefins styrene (Table 3, entry 7) and *p*-chlorostyrene (Table 3, entry 8). Low yields, but in comparison to alternative systems still respectable TONs, were obtained for α-methylstyrene (Table 3, entry 9), methyl methacrylate (Table 3, entry 10), and 1-decene (Table 3, entry 11).

Subsequently, the ATRA reaction of polychlorinated esters to olefins was investigated. Tri- and dichlorinated ethyl acetate was efficiently added to styrene and methyl methacrylate at room temperature. By using an olefin/Ru ratio of 1000:1, the addition products were obtained in good yields after 24 or 48 h (Table 4). The catalyst concentration can be as low as 0.02 mol%, as shown by the addition of $CHCl_2CO_2Et$ to styrene (Table 4, entry 6), which gave the product in a yield of 90% after 24 h (TON = 4500). This result compares very favorably to other synthetic procedures. The addition of CCl_3CO_2Et to styrene, for example, gave a yield of 57% when Grubbs catalyst $[RuCl_2(PCy_3)_2(=CHPh)]$ (5 mol%) was used at 75°C (TON = 11).[5f] For the same reaction, a TON of 238 has been reported for catalyst **5**, but a reaction temperature of 120°C was employed.[14] It should be noted that the products are synthetically interesting precursors because they can be cyclized to form lactones.[5f,15]

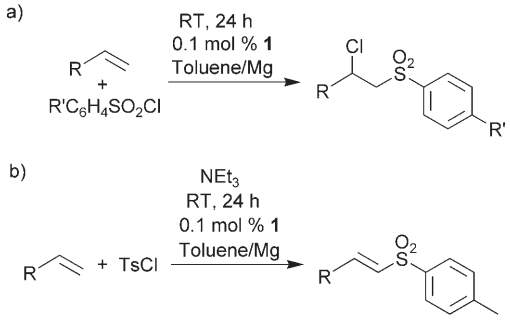
The radical addition of sulfonyl chlorides to olefins has been studied extensively by Kamigata and co-workers.[16,17] Typically, these reactions were carried out at 60 to 120°C with **5** (1 mol%). The reaction of *p*-toluenesulfonyl chloride (TsCl) with styrene in the presence of NBu_3, for example, gave (*E*)-β-(*p*-toluenesulfonyl)styrene in a yield of 86%

Table 4. ATRA reaction of α-chlorinated esters to olefins catalyzed by complex **1** in the presence of Mg.[a]

Entry	Olefin	R–Cl	[Ru]/[Olefin]	*t* [h]	Conv.[b] [%]	Yield[c] [%]
1	styrene	CCl_3CO_2Et	1:1000	48	100	94
2	*p*-chlorostyrene	CCl_3CO_2Et	1:1000	48	100	91
3	α-methylstyrene	CCl_3CO_2Et	1:1000	48	100	82
4	methyl methacrylate	CCl_3CO_2Et	1:1000	48	71	67
5	styrene	$CHCl_2CO_2Et$	1:1000	24	100	97
6	styrene	$CHCl_2CO_2Et$	1:5000	24	100	90
7	*p*-chlorostyrene	$CHCl_2CO_2Et$	1:1000	24	100	95
8	α-methylstyrene	$CHCl_2CO_2Et$	1:1000	24	100	94
9	methyl methacrylate	$CHCl_2CO_2Et$	1:1000	24	100	84

[a] The reactions were performed at room temperature in the presence of activated Mg powder (100 mg) in toluene saturated with D_2O as the solvent (total volume = 1000 μL, [olefin] = 1.38 M). [b] The conversion is based on the consumption of the olefin. [c] The yield is based on the formation of the product as determined by ^1H NMR spectroscopy by using the internal standard 1,4-bis(trifluoromethyl)benzene (270 mM).

after 72 h (1 mol% **5**, 60°C).[17h] In the absence of base, the 1:1 addition product 1-[(2-chloro-2-phenylethyl)sulfonyl]-4-methylbenzene could be obtained in a yield of 92% after 40 h, but a higher temperature of 120°C was required.[17f] Alternatively, coupling sulfonyl chlorides to olefins can be performed with CuCl (1–2 mol%) in the presence of Et_3NHCl at 80 to 100°C.[18] Owing to the acidic conditions, the 1:1 addition products were obtained and not the α,β-unsaturated sulfones. By using a catalyst system that comprised of complex **1** and Mg, it was possible to couple arenesulfonyl chlorides to olefins at room temperature with only 0.1 mol% Ru catalyst (Scheme 2a, Table 5). Interestingly,



Scheme 2. ATRA of *p*-toluenesulfonyl chloride to styrene catalyzed by complex **1** in the presence of Mg.

smaller amounts of Mg (1.0 equiv with respect to styrene) were found to be advantageous for this type of ATRA reaction. Similar to that observed for reactions with **5**, the addition of NEt_3 leads to a clean conversion of the monoadduct to the unsaturated sulfone in situ. This was evidenced by the reaction of styrene with TsCl, in which the product, (*E*)-β-(*p*-toluenesulfonyl)styrene, was isolated in a yield of 96% after 24 h (Scheme 2b).

From a synthetic point of view, intramolecular ATRA reactions are the most interesting transformations. These reactions are generally referred to as atom-transfer radical cyclizations (ATRC). As mentioned above, Ru^{II} catalysts have been used for this purpose,[3] but Cu^{I}-based catalysts are also highly successful in this context.[3,19] Recent developments include the investigation of sequential ring-closing metathesis/ATRC reactions,[20] the use of an ATRC reaction as a key step for the synthesis of natural products[21] or novel aromatic compounds,[22] and the study of immobilized catalysts.[23]

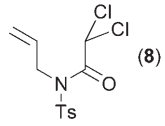
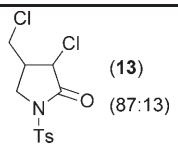
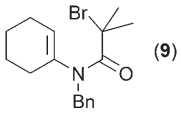
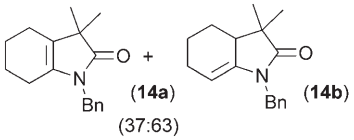
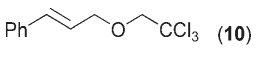
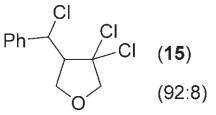
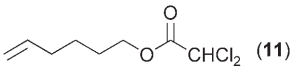
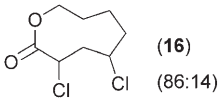
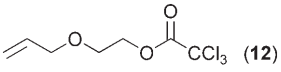
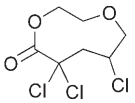
The cyclization of *N*-allyltrichloroacetamides to give chlorinated γ-butyrolactams is one of the most studied ATRC reaction and various Cu and Ru complexes are able to catalyze this reaction.[3,19] *N*-Allyldichloroacetamides are less reactive substrates and when standard catalysts, such as CuCl/bipy[24] or $[RuCl_2(PPh_3)_3]$,[25] are used then high reaction temperatures and/or high catalyst loadings are required. Recently, some Ru catalysts that allow the reaction to be carried out at room temperature have been described.[5a,c,24] For the cyclization of *N*-allyl-*N*-tosyldichloroacetamide (**8**), the most active Ru catalyst known to date is the methoxy-bridged dimer $[\{RuCp^*(OMe)\}_2]$ in combination with pyridine as an activating ligand. By using 5 mol% of this dimer (10 mol% Ru), it is possible to cyclize **8** in excellent yields within four hours. One drawback from a preparative point of view, however, is the high sensitivity (i.e., air and moisture sensitivity) of $[\{RuCp^*(OMe)\}_2]$.[26] When we investigated the cyclization of **8** by using 5 mol% of air-stable complex **1** in combination with Mg, we found that the corresponding γ-butyrolactam could be obtained with an isolated yield of 94% after 4 h (Table 6, entry 1). Almost quantitative cyclization of **8** (95% yield, as determined by NMR spectroscopy) was possible with a catalyst concentration of only 2.5 mol%, but longer reaction times of eight hours were required.

Table 5. ATRA reaction of sulfonyl chlorides to olefins catalyzed by complex **1** in the presence of Mg.[a]

Entry	Olefin	R	Conv.[b] [%]	Yield[c] [%]
1	styrene	p-$CH_3C_6H_4$	100	98
3	*p*-methoxystyrene	p-$CH_3C_6H_4$	100	98
4	α-methylstyrene	p-$CH_3C_6H_4$	100	97
5	methyl methacrylate	p-$CH_3C_6H_4$	75	69
6	styrene	p-$CH_3OC_6H_4$	100	98
7	*p*-methoxystyrene	p-$CH_3OC_6H_4$	100	97
8	α-methylstyrene	p-$CH_3OC_6H_4$	100	97
9	methyl methacrylate	p-$CH_3OC_6H_4$	65	52

[a] The reactions were performed at room temperature in the presence of activated Mg powder (10 mg) and 0.1 mol% of complex **1** in toluene saturated with D_2O as the solvent (total volume = 1000 μL, [olefin] = 0.44 M; $[RSO_2Cl] = 0.52$ M. [b] The conversion is based on the consumption of the olefin. [c] The yield is based on the formation of the product as determined by ^1H NMR spectroscopy after 24 h by using the internal standard mesitylene (90 mM).

Table 6. ATRC reactions catalyzed by complex **1** in the presence of Mg.[a]

Entry	Substrate	Product(s)	[Ru] [mol %]	t [h]	T [°C]	Conv. [%]	Yield[b] [%]
1	 (**8**)	 (**13**) (87:13)	5	4	RT	100	94
2	 (**9**)	 (**14a**) (37:63) (**14b**)	0.05	9	RT	100	94
3	 (**10**)	 (**15**) (92:8)	0.5	9	RT	98	89
4	 (**11**)	 (**16**) (86:14)	1	48	60	91	67
5	 (**12**)	 (**17**)	1	48	80	89	66

[a] The reactions were performed in the presence of activated Mg powder in toluene saturated with D_2O (entries 2, 3), CH_2Cl_2 (entry 1) or 1,2-dichloroethane (entries 4, 5) as the solvent ([substrate] = 0.14 M). For substrate **9** (entry 2) one equivalent of NEt_3 was added to the reaction mixture. [b] Isolated Yield.

The 5-*endo* cyclization reaction of α-bromo enamides has been investigated by Clark et al.[23,27] They found that tertiary bromo enamides, such as **9**, can be cyclized at room temperature by using a combination of CuBr (30 mol %) and an activating ligand (30 mol %), such as tris(*N*,*N*-2-dimethylamino)ethylamine (Me_6-Tren). It was suggested that this formal Heck-type reaction proceeds through a radical–polar crossover mechanism with elimination of HBr.[27] By using complex **1** and Mg instead of CuBr and Me_6-Tren, it is possible to reduce the catalyst concentration to 0.05 mol % without compromising the yield of the reaction (Table 6, entry 2).

The ATRC reactions of ethers were studied by Ram and Charles.[22b] They reported that 2,2,2-trichloroethyl ether **10** could be efficiently cyclized at 80 °C by using CuCl/bipy (30 mol %) as the catalyst. We found that this reaction could be performed with complex **1** (0.5 mol %) at room temperature (Table 6, entry 3). Furthermore, whereas the Cu-catalyzed reaction proceeds with low diastereoselectivity, we were able to obtain a high selectivity of 92:8.

Transition-metal-catalyzed ATRC reactions can also be used for the synthesis of macrocyclic compounds. Pirrung and co-workers used a combination of CuCl and bipyridine to generate various medium-sized lactones.[28] The cyclization of dichloroester **11** was performed with a Cu concentration of 30 mol % at 80 °C to give the nine-membered lactone **16** in a yield of 57 % with a diastereoselectivity of 70:30. We observed comparable yields, but an improved selectivity (86:14), by using a Ru concentration of only 1 mol % at 60 °C (Table 6, entry 4).

The ATRC reaction of polyoxalkenyl trichloroesters has been studied by Verlhac et al.[29] They performed the cyclization of **12** at 80 °C by using 10 mol % of Cu^I and Fe^{II} complexes. By using $FeCl_2$/N^1-[2-(dimethylamino)ethyl]-N^1,N^2,N^2-trimethylethane-1,2-diamine as the catalyst, they were able to obtain **17** in a yield of 56 %, whereas poor yields were observed for the Cu^I catalyst tested. It is interesting to note that the addition of Fe powder increased the reaction rate for this reaction although the final yield was not affected. Our method, which involves a combination of complex **1** and Mg, compares very favorably to these results. Macrocycle **17** could be obtained in a yield of 66 % by using only 1 mol % of Ru (Table 6, entry 5).

Conclusion

We have described a new procedure for ATRA and ATRC reactions, which uses a combination of complex **1** and magnesium as the catalyst. The novel system offers a number of advantages: 1) catalyst precursor **1** is air-stable and easy to generate by mixing commercially available $[(RuCl_2Cp^*)_2]$ with PPh_3, 2) the Mg co-catalyst is cheap, nontoxic, and can be separated by filtration, 3) the procedure is general because good results were obtained for a diverse set of substrates, 4) the reactions can be performed with very low catalyst concentrations under mild conditions, and 5) the mild reaction conditions allow good diastereoselectivities to be obtained for ATRC reactions. Given these advantages, it is likely that this procedure will find various applications in organic synthesis.

Experimental Section

General: Complexes $[(RuCl_2Cp^*)_2]$,[30] **1**,[10b] **2**,[30] **5**,[31] **6**,[5b] and **7**[32] were prepared according to literature procedures. Complex **3** was synthesized by treating $[(RuCl_2Cp^*)_2]$ with PBu_3 (2 equiv) in CH_2Cl_2. Syntheses of all complexes were performed under an atmosphere of dry nitrogen by using standard Schlenk techniques. Mg powder (>99%) was purchased from Fluka and was agitated by means of a stirring bar under an atmosphere of dry nitrogen for 10 d before use. All ATRA and ATRC reactions were performed under an atmosphere of dry nitrogen. The solvents and the commercially available substrates were distilled from the appropriate drying agents and stored under nitrogen. ^1H and ^{13}C NMR spectra were recorded by using a Bruker Advance DPX 400 spectrometer with the residual protonated solvents (^1H, ^{13}C) as internal standards. All spectra were recorded at room temperature. *N*-Allyl-*N*-4-toluenesulfonyl-2,2-dichloroacetamide (**8**),[33] *N*-benzyl-2-methyl-2-bromo-*N*-cyclohexyl-1-enylpropionamide (**9**),[23b] [(2,2,2-trichloroethoxy)prop-1-enyl]benzene (**10**),[22b] hex-5-enyl-2,2-dichloroacetate (**11**),[28] and 2-(allyloxy)ethyl-2,2,2-trichloroacetate (**12**)[29] were prepared according to literature procedures.

General procedure for ATRA of CCl_4 to olefins: The desired amount of a stock solution of complex **1** in toluene was added to a 1.5 mL vial that contained Mg powder (100 mg) and the mixture was stirred for 10 min. D_2O (20 μL) was added to a freshly prepared stock solution of the olefin, CCl_4, and the internal standard 1,4-bis(trifluoromethyl)benzene in toluene and the mixture was shaken for 1 min to saturate the solution with D_2O. This stock solution (950 μL) was added to the vial and the total volume was increased to 1000 μL with toluene ([olefin] = 1.38 M, [CCl_4] = 5.52 M, [internal standard] = 270 mM). The resulting solution was stirred at room temperature and after a given time, a sample (20 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (500 μL), and analyzed by ^1H NMR spectroscopy.

General procedure for ATRA of $CHCl_3$ to olefins: The desired amount of a stock solution of complex **1** in $CHCl_3$ was added to a 1.5 mL vial that contained Mg powder (100 mg) and the mixture was stirred for 10 min. D_2O (20 μL) was added to a freshly prepared stock solution of the olefin and the internal standard 1,4-bis(trifluoromethyl)benzene in $CHCl_3$ and the mixture was shaken for 1 min to saturate the solution with D_2O. This stock solution (875 μL) was added to the vial and the total volume was increased to 1000 μL with $CHCl_3$ ([olefin] = 1.38 M, [internal standard] = 270 mM). The resulting solution was stirred at room temperature and after a given time, a sample (20 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (500 μL), and analyzed by ^1H NMR spectroscopy.

General procedure for ATRA of chlorinated esters to olefins: The desired amount of a stock solution of complex **1** in toluene was added to a 1.5 mL vial that contained Mg powder (100 mg) and the mixture was stirred for 10 min. D_2O (20 μL) was added to a freshly prepared stock solution of the chlorinated ester, the olefin, and the internal standard 1,4-bis(trifluoromethyl)benzene in toluene and the mixture was shaken for 1 min to saturate the solution with D_2O. This stock solution (700 μL) was added to the vial and the total volume was increased to 1000 μL with toluene ([olefin] = 1.38 M, [$CXCl_2CO_2Et$] = 2.76 M, [internal standard] = 270 mM). The resulting solution was stirred at room temperature and after a given time, a sample (20 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (500 μL), and analyzed by ^1H NMR spectroscopy.

General procedure for ATRA of TsCl to olefins: The desired amount of a stock solution of complex **1** in toluene was added to a 1.5 mL vial that contained Mg powder (10 mg) and the mixture was stirred for 10 min. D_2O (20 μL) was added to a freshly prepared stock solution of the olefin, TsCl, and the internal standard mesitylene in toluene and the mixture was shaken for 1 min to saturate the solution with D_2O. This stock solution (800 μL) was added to the vial and the total volume was increased to 1000 μL with toluene ([olefin] = 0.44 M, [TsCl] = 0.52 M, [internal standard] = 90 mM). The resulting solution was stirred at room temperature and after a given time, a sample (20 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (500 μL), and analyzed by ^1H NMR spectroscopy.

General procedure for ATRC reactions: The desired amount of a stock solution of complex **1** was added to a 20 mL Schlenk flask that contained Mg powder (1 g) and the mixture was stirred for 10 min. D_2O (200 μL) was added to a freshly prepared stock solution of the substrates (CH_2Cl_2 for **8**, toluene for **9** and **10**, and 1,2-dichloroethane for **11** and **12**) and the mixture was shaken for 1 min to saturate the solution with D_2O. In the case of substrate **9**, one equivalent of NEt_3 was added to the solution. This stock solution (8.0 mL) was added to the reaction flask and the total volume was increased to 10 mL with the respective solvent (final conc.: [substrate] = 0.14 M). The resulting solution was stirred at room temperature (**8**, **9**, **10**), at 60 °C (**11**), or at 80 °C (**12**). After a given time, the crude reaction mixture was filtered and the solvent was removed in vacuum. The product was then purified by column chromatography and characterized by NMR spectroscopy.

For the analytical data of the compounds **13**, **14**, **16**, **17** see references [5a, 27–29]. 3,3-Dichloro-4-[chloro(phenyl)methyl]tetrahydrofuran (**15**) was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 97:3); ^1H NMR (400 MHz, $CDCl_3$): (S,S) $\delta = 5.19$ (d, 1H), 4.49 (t, 1H), 4.32 (d, 1H), 4.20 (d, 1H), 4.12 (t, 1H), 3.71 ppm (m, 1H); (S,R) $\delta = 5.13$ (d, 1H), 4.37 (d, 1H), 4.27 (d, 1H), 3.63–3.41 ppm (m, 3H).

Crystallographic investigations: Single crystals of complex **1** were obtained by slow diffusion of pentane into a solution of **1** in benzene. The relevant details of the crystal, data collection, and structure refinement are listed in Table 7. Diffraction data were collected by using $Mo_{K\alpha}$ radiation by using a Bruker APEX II CCD instrument. Data were reduced by EvalCCD.[34] Absorption correction was applied using a semiempirical method.[35] The structure was refined by using the full-matrix least-squares method on F^2 with all non-hydrogen atoms anisotropically defined. The hydrogen atoms were placed in calculated positions by using the "riding model" with $U_{iso} = a^* U_{eq}$ (in which U_{iso} is the isotropic displacement parameter, U_{eq} is the equivalent isotropic displacement, and a is 1.5 for methyl hydrogen atoms and 1.2 for other atoms). Structure so-

Table 7. Crystallographic data for complex **1**.

	1·1.5 C_6H_6
Empirical formula	$C_{37}H_{39}Cl_2PRu$
Molecular weight [g mol^{-1}]	686.62
Crystal size [mm^3]	$1.06 \times 0.47 \times 0.30$
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	8.5339(10)
b [Å]	17.483(2)
c [Å]	21.902(2)
α [°]	90
β [°]	91.536(7)
γ [°]	90
V [Å^3]	3266.5(7)
Z	4
ρ_{calcd} [g cm^{-3}]	1.396
T [K]	100(2)
Absorption coefficient [mm^{-1}]	0.717
θ range [°]	3.34 to 25.02
Index ranges	$-10 \rightarrow 10$, $-20 \rightarrow 20$, $-26 \rightarrow 26$
Reflections collected	54442
Independent reflections	5748 ($R_{int} = 0.0340$)
Absorption correction	semiempirical
Max. and min. transmission	1.0000 and 0.7599
Data/restraints/parameters	5748/0/370
Goodness-of-fit on F^2	1.153
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0221$, $wR_2 = 0.0443$
R indices (all data)	$R_1 = 0.0276$, $wR_2 = 0.0466$
Largest diff. peak/hole [eÅ^{-3}]	0.381/−0.344

lution, refinement, and geometrical calculations were carried out by using the SHELXTL program.[36] CCDC-641174 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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