



Cycloruthenated complexes as homogeneous catalysts for atom-transfer radical additions

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ABSTRACT

Various cycloruthenated complexes were used as homogeneous catalysts for the atom-transfer radical addition of polyhalogenated compounds to several olefinic substrates. Yields obtained through conventional or microwave heating could reach high values (up to 98% with CBrCl_3 and 88% with CCl_4).

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The Kharasch reaction is an efficient method for the formation of C–C bonds.¹ It has encountered renewed interest within the last decade because the high reactivity of radical intermediates can be tamed by transition metal catalysts; such metal-catalysed additions of radicals (e.g., originated from polyhalogenated compounds) onto olefins are known as atom-transfer radical addition (ATRA) reactions.² Among these ATRA catalysts, ruthenium complexes are now widely used,³ including many half-sandwich complexes.

Besides, cycloruthenated complexes are easy to synthesise in good yield, and they have proved to be markedly robust, the metal-carbon bond being stabilized by chelation.⁴ We have been interested lately in their properties as hydrogen transfer catalysts.⁵ However, examples of applications of cycloruthenated complexes in other domains of homogeneous catalysis remain relatively scarce.⁴ In the field of radical processes, Alexandrova et al. have recently reported the successful use of cycloruthenated complexes in atom-transfer radical polymerisation catalysis.⁶

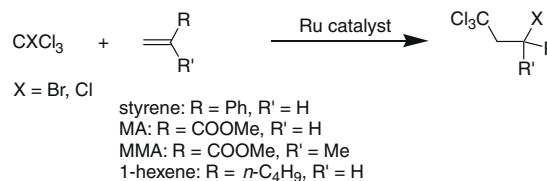
We will report hereafter some unprecedented properties of cycloruthenated complexes as catalyst precursors in the field of ATRA reactions. The reaction consisted in the addition of bromotrichloroethane or carbon tetrachloride with various olefins (Scheme 1).

A first set of catalytic tests were run using reactive CBrCl_3 as a radical addition reagent and styrene as an olefinic substrate (Table 1); the experimental conditions (molar ratios) reported by Kamigaito et al.⁷ were followed. The yields and conversions were determined

after a 6 h reaction at 80 °C. We used cycloruthenated complexes belonging to the library shown in Scheme 2 as ATRA catalysts; their synthesis has been reported previously (see Supplementary data). Overall we observed that the yield and conversion for a given catalyst were nearly the same, the difference between both figures being less than 5% except for catalyst **2c** (entry 7). We can therefore conclude that side reactions such as radical polymerisation⁸ of styrene occur very little.

All the catalysts except **5b** were active, with yields ranging from 42% to 98%. The effect of the bridging ligand X in the **5** series is remarkable: the presence of a bridging hydroxo ligand (**5a**, entry 14) instead of a chloro (**5b**, entry 15) makes the complex catalytically active. The other μ -hydroxo, μ -chloro ruthenacyclic dimer **6** exhibits an activity similar to that of **5a**.

Within the subfamily of mononuclear ruthenium complexes, the best candidates for ATRA were the η^6 -arene neutral complexes derived from *N,N*-dimethylbenzylamines (DMBAs) **1a** and **1d** (en-



Scheme 1. Ruthenium-catalysed Kharasch addition of polyhalogenated compounds to olefins.

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Table 1
Addition of bromotrichloromethane to styrene catalysed by cycloruthenated complexes^a

Entry	Catalyst	Conversion ^b (%)	Yield ^b (%)
1	1a	99	98
2	1b	56	56
3	1c	43	42
4	1d	98	98
5	2a	67	67
6	2b	49	49
7	2c	76	66
8	2d	60	59
9	2e	88	88
10	3	83	83
12	4a	59	58
13	4b	72	70
14	5a	70	70
15	5b	— ^c	— ^c
16	6	60	56

^a Reaction conditions: styrene (1.4 mmol), CBrCl₃ (4.2 mmol), catalyst (0.01 mmol), standard (0.14 mmol), 80 °C, 6 h (see experimental details in Supplementary data); yield of uncatalysed reaction (blank) is 5%.

^b Conversions and yields were based on the olefin, and were determined by ¹H NMR using tetraline as an internal standard.

^c Traces.

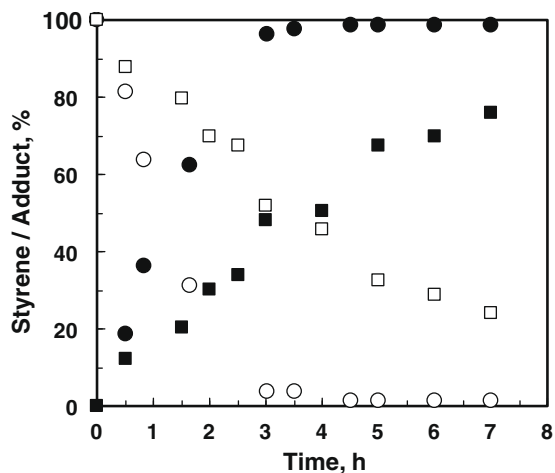


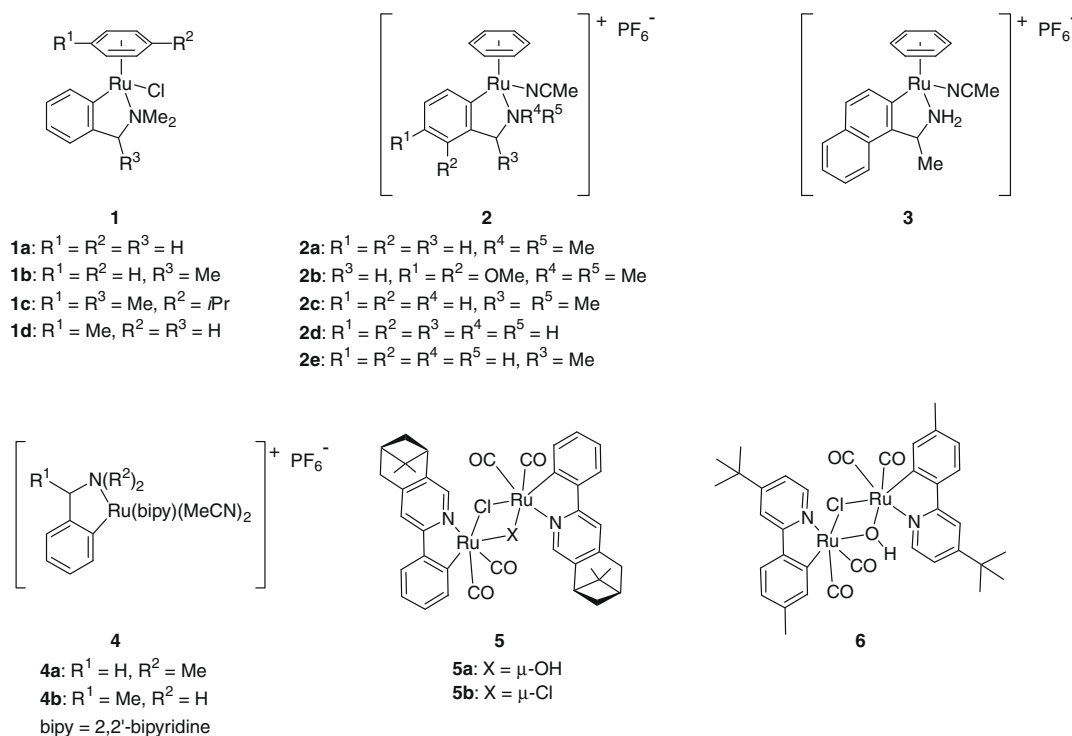
Figure 1. Styrene (○,□) and adduct (●,■) versus time for the addition of bromotrichloromethane to styrene catalysed by complexes **1a** (●,○) and **2e** (■,□) at 80 °C (conventional heating). The reaction conditions were as listed in Table 1, except the reaction mixture was evenly charged into nine glass tubes (see Supplementary data). Determination of conversions and yields: see Table 1.

tries **1** and **4**), which led almost quantitatively to the 1:1 adduct. Another kind of catalysts that led to high chemical yields (>80%) were cationic η⁶-benzene complexes resulting from cycloruthenation of primary benzylic amines, viz. **2e** and **3** (entries 9 and 10). By contrast with these cyclometallated tertiary and primary amines, the cycloruthenated secondary amine **2c** (NHMe analogue of **2e**) afforded a lower yield.

Switching from **1a** to the cationic analogue **2a** afforded a lower yield (67%, entry 5); according to the literature on ATRA ruthenium catalysts, sometimes the catalytic performance decreased similarly upon abstraction of a chloro ligand,⁹ but the reverse effect was also reported.¹⁰ In our case, we cannot interpret the comparison

between neutral and cationic cyclometallated complexes only as a general positive effect of increased electron density on the metal, because conversely the electron-donating methoxy substituents on the metallated phenyl group of complex **2b** diminished the yield with regard to **2a** (entries 5 and 6). By contrast, Demonceau et al. had observed a positive influence of electron-donating groups on phosphine ligands in Ru-catalysed ATRA.¹¹ In accordance with our own findings, no correlation was found between the reducing power of cycloruthenated complexes and their ATRP catalytic activity.⁶

We noticed that the bipy-coordinated complexes **4a** and **4b** were less efficient than their half-sandwich analogues, respec-



Scheme 2. Cycloruthenated ATRA catalysts.

Table 2
Addition of bromotrichloromethane to various alkenes catalysed by cycloruthenated complexes^a

Entry	Substrate	Catalyst	T (°C)	Conversion (%)	Yield (%)
1	MMA	1a	45 ^b	1	1
2	MMA	1a	60 ^b	99	63
3	MMA	1a	80 ^b	99 ^c	99 ^c
4	MMA	1a	135 ^d	100	99
5	MMA	1d	60 ^b	99	56
6	MMA	1d	80 ^b	94	63
7	MMA	1d	135 ^d	100	98
8	MMA	3	135 ^d	100	81
9	MA	1a	60 ^b	99	89
10	MA	1a	80 ^b	96	94
11	MA	1d	60 ^b	58	18
12	MA	1d	80 ^b	69	51
13	MA	2e	80 ^b	88	30
14	MA	3	80 ^b	99	80
15	1-Hexene	1a	80 ^b	44	44
16	1-Hexene	1d	80 ^b	45	43
17	1-Hexene	3	80 ^b	30	30

^a Reaction conditions: alkene (1.4 mmol), CBrCl₃ (4.2 mmol), catalyst (0.01 mmol), standard (0.14 mmol); see experimental details in [Supplementary data](#). Determination of conversions and yields: see [Table 1](#).

^b Conventional heating, *t* = 6 h unless otherwise stated; we found that no reaction took place without catalyst under any of those conditions.

^c Conversion and yield after *t* = 3 h.

^d Microwave reactor, *t* = 30 min; yield of uncatalysed reaction (blank) is 10%.

tively, **2a** and **2e** (entries 12 and 13 vs 5 and 9). However, from these observations in particular and from all data listed in [Table 1](#) in general, it is difficult to rationalise the influence on the catalytic efficiency of various factors (charge of the complex, nature of ancillary ligands, nature of substituents on the cyclometallated molecule, etc.). Some contradictory trends were even observed; for instance, comparison between **1a** and **1b** showed that a methyl substituent in benzylic position was detrimental to the yield in the DMBA series, but reversibly it had a positive effect on the yield in the cationic cycloruthenated benzylamine series (**2d** vs **2e**).

We have represented in [Figure 1](#) the kinetic profiles of the Kharasch addition of CBrCl₃ on styrene catalysed by **1a** and **2e** at 80 °C. They confirm that the conversions and yields were practically equal over time with both catalysts. The reaction catalysed by **1a** was over within 3 h, whereas **2e** was slower; turn-over frequencies (TOF) of, respectively, 54 h⁻¹ and 21 h⁻¹ were estimated for **1a** and **2e** from the curves shown in [Figure 1](#). The final yield after 6 h reaction with **2e** (75%) was slightly lower than the yield (88%) mentioned in [Table 1](#); this may be due to minor differences between

the experimental procedures (absence of stirring in the conditions shown in [Fig. 1](#)).

The ability of cycloruthenated complexes to catalyse Kharasch additions of CBrCl₃ on other substrates, viz. methyl acrylate (MA), methyl methacrylate (MMA) and 1-hexene, was then evaluated ([Table 2](#)). The DMBA-catalysts **1a** and **1d**, and also the cationic cycloruthenated primary amines **2e** and **3** were selected for that purpose. Reactions at 80 °C led to yields ranging from 30% to 99%; there was often a gap between conversion and yield, indicating substantial oligomerisation or polymerisation.

As expected, yields were higher overall with substrates MA and MMA than with 1-hexene. We noticed that catalyst **1a**, which led to an almost quantitative conversion of MMA into the CBrCl₃-adduct within 3 h only at 80 °C (entry 3), was still active when the temperature was lowered to 60 °C (63% yield in 6 h, entry 2). It is worth noting that using MA as the substrate, the yield at 80 °C reached 94% with **1a**, whereas it was only 51% with **1d** (entries 10 and 12), although both catalysts differ slightly; furthermore, decreasing the temperature to 60 °C was not very detrimental to the yield with **1a** (89%, entry 9), but it was so with **1d** (18%, entry 11).

Demonceau et al. have reported the use of microwave irradiation as the heating source in ATRA reactions with CCl₄ using half-sandwich ruthenium catalysts.¹² This device proved to be a convenient way to provide fast heating of the reaction medium. Thus, we have also used it to reach higher reaction temperatures easily. Indeed the reaction of MMA with CBrCl₃ proceeded with excellent yields (81%–99%) within a short time (30 min, entries 4, 7 and 8).

We then tried this method with the less reactive polyhalogenated species CCl₄ ([Table 3](#)). Initial attempts of addition of CCl₄ to various olefins by conventional heating to 80 °C had not been very successful, as long as five days heating was necessary to attain reasonable yields and conversions. Easily polymerisable¹² substrates such as styrene (catalyst **3**, entry 1) and MMA (catalyst **1d**, entry 6) led to high conversions (92% and 82%) but negligible yields. The yield of addition of CCl₄ on styrene reached much higher values (23–75%) within shorter times (0.5–1 h) when the reaction medium was submitted to a temperature of 135 °C in a microwave oven (entries 2–5). At first sight it seemed surprising that the yield could increase to 75% at *t* = 1 h whereas the conversion was already 100% at *t* = 0.5 h (entries 2 vs 3); this was probably due to the fact that in the oven, the reaction mixture was not frozen immediately after the reaction time was elapsed, and the substrate may have undergone side reactions during the period of time when temperature decreased. A similar phenomenon happening at the beginning of the microwave-assisted ATRA reaction has been reported previously.¹²

Table 3
Addition of carbon tetrachloride to various alkenes catalysed by cycloruthenated complexes^a

Entry	Substrate	Catalyst	T (°C)	Reaction time (h)	Conversion ^b (%)	Yield ^b (%)
1	Styrene	3	80 ^b	120	92	2
2	Styrene	3	135 ^c	0.5	100	51
3	Styrene	3	135 ^c	1	100	75
4	Styrene	1d	135 ^c	0.5	68	23
5	Styrene	1d	135 ^c	1	83	32
6	MMA	1d	80 ^b	120	82	0
7	MMA	1d	135 ^c	0.5	98	88
8	MMA	3	135 ^c	0.5	48	2
9	1-Hexene	1d	80 ^b	120	73	73
10	1-Hexene	2e	80 ^b	120	46	46
11	1-Hexene	1d	135 ^c	0.5 ^d	59	59
12	1-Hexene	3	135 ^c	0.5 ^d	21	21

^a Reaction conditions: alkene (1.4 mmol), CCl₄ (4.2 mmol), catalyst (0.01 mmol), standard (0.14 mmol); see experimental details in [Supplementary data](#). We found that no 1:1 ATRA adduct was formed without catalyst under any of those conditions, unless otherwise stated. Determination of conversions and yields: see [Table 1](#).

^b Conventional heating.

^c Microwave reactor.

^d Yield of uncatalysed reaction under those conditions was 5%.

It is striking to note that using MMA as the substrate, microwave heating led to a very good yield (88%, entry 7) using catalyst **1d**, but it led to a yield of 2% only using catalyst **3** (entry 8); by contrast, **3** was superior to **1d** with styrene as the ATRA substrate. Overall, these figures showed that under microwave conditions, unwanted chemical processes were avoided and the ATRA reaction was often favoured.

With the non-activated substrate 1-hexene, the final yield in Kharasch product was always equal to the conversion, indicating that no polymerisation occurred (which is often expected with this kind of substrate). Under conventional heating conditions, a good yield (73%) could be reached after 5 days heating at 80 °C (entry 9). The reaction time was reduced to 0.5 h under microwave conditions with fair yields (21 and 59%, respectively, entries 11 and 12).

Although we have implemented no mechanistic investigations on ruthenacycle-catalysed Kharasch reactions so far, it is likely that the reaction starts with the abstraction of X from CXCl₃ that yields a Ru^{III}-X transient species and a reactive ·CCl₃ radical, like other Ru-catalysed atom-transfer radical additions.³ It has often been proposed and discussed in the literature on ATRA¹³ or ATRP^{6a} that the active species would be an unsaturated ruthenium complex issued from the decoordination of one of the ligands. With our own catalysts, this ligand is probably a chloro, a hydroxo or an acetonitrile.

In conclusion, these preliminary investigations have shown that cycloruthenated complexes exhibit interesting catalytic activities in the field of ATRA reactions, even with a moderately reactive substrate such as 1-hexene. They represent a new advancement in the field of organic transformations catalysed by metallacycles. We noticed a beneficial effect of microwave irradiation similar to the one reported previously with other ruthenium catalysts;¹² this procedure considerably shortened the reaction times and could lead to very good yields with CBrCl₃ or even CCl₄. Our preliminary findings have opened a way towards potentially interesting applications, and they encourage us to extend the library of ATRA catalysts to other complexes, for example, cycloruthenated phosphines or carbenes. Further work in asymmetric Kharasch reactions is now under progress using chiral cycloruthenated complexes; these proved successful in the past with other asymmetric catalytic reactions, such as the reduction of ketones via hydrogen transfer.^{4,5}

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Supplementary data

Supplementary data (catalysts synthesis, experimental procedures) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.011.

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