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Greatly improved activity in ruthenium catalysed butanone synthesis

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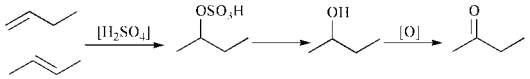
***In situ* mixing of ruthenium trichloride with one equivalent of 1,10-phenanthroline yields a highly active catalyst for synthesis of butanone from buta-1,3-diene.**

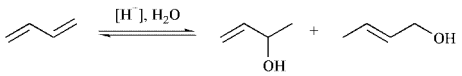
Butanone is an industrial solvent, nowadays produced on a Mton scale per year.[1] It is presently prepared from butenes in a three-step process according to eqn. (1).[2] The use of large



(1)

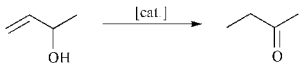
quantities of concentrated sulfuric acid, which need to be reconcentrated after the second step, make this process in principle less desirable from an environmental and an economical point of view. Therefore, new synthetic strategies have been developed in recent years.

Butadiene is readily obtained from naphtha cracker C_4-streams and its two double bonds make it susceptible towards electrophilic addition. Routes to butanal using butadiene *via* addition of amines[3] or alcohols,[4] followed by isomerisation of the allylic double bond and hydrolysis, have been patented. Acid-catalysed hydration of butadiene gives rise to two regioisomeric alcohols [eqn. (2)], but-3-en-2-ol and but-2-en-1-ol, in



(2)

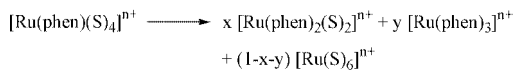
an equilibrium that lies heavily on the left-hand side. The former alcohol can be isomerised to butanone [eqn. (3)].[5] In a one-pot



(3)

synthesis, the thermodynamically favourable formation of butanone avoids an extensive (and thus costly) butadiene recycle. Unfortunately, almost all catalysts capable of allylic alcohol isomerisation are strongly poisoned by butadiene.

In the early 1990s, the synthesis of butanone from butadiene catalysed by a mixture of $[Ru(acac)_3]$ (Hacac = pentane-2,4-dione), 1,10-phenanthroline (phen) and a Brønsted acid in water was published.[6] However, the reported cumulative turn over number (TON) of 1200 in 32 h is not sufficiently high to be economically interesting. The limited TON is due to catalyst deactivation *via* two pathways: ligand redistribution and metal reduction, which result in inactive $[Ru(phen)_2(S)_2]^{2+}$ (S = solvent) and $[Ru(phen)_3]^{2+}$ species [eqn. (4)].[6,7] Yet, despite



(4)

considerable effort,[8] until now no catalyst was found to be more active.

Strongly coordinating anions like chlorides were originally thought[6] to hamper catalysis by blocking vital coordination sites. In fact, $[RuCl_3{\cdot}xH_2O]$ in combination with two equivalents of 2,2′-bipyridine (bpy) gave only low activity. However, during the course of our studies,[7] it was found that the presence of chloride ions in some cases had a promoting effect. Here, we report the reinvestigation of $RuCl_3$ as catalyst precursor in the synthesis of butanone from butadiene.

The results of *in situ* experiments for the direct conversion of butadiene to butanone are shown in Table 1.† The blank experiments shown in entries 1 and 2 confirm the need for both ruthenium and phenanthroline. Especially the amount of ligand is crucial. Whereas $RuCl_3$ with two equivalents of phen (entry 5) gives only moderate activity that is comparable to previous results (entry 3), $RuCl_3$ with one equivalent phen is by far superior as is shown in entry 4. This result demonstrates clearly that with a chloride-containing precursor high activity can be obtained, contrary to earlier ideas. Mixed with one equivalent of bipyridine, $RuCl_3$ is only as active as $Ru(acac)_3$ with one phen (entry 6).

Not only are initial rates higher, the $RuCl_3$–phen system surpasses the $Ru(acac)_3$–phen system if TONs are considered as well. After a mere two hours, 1400 turnovers can be attained. Importantly, the $RuCl_3$–phen system is exceedingly selective. The most important side products in this reaction are the Diels–Alder dimer of butadiene (vinyl cyclohexene) and butenes together with methyl vinyl ketone, but their formation can be reduced to less than 1% with a suitably low initial butadiene loading of the autoclave. Thus, high TONs can be reached with a minimum amount of side products. This is demonstrated by an experiment in which the amount of butadiene is fed into the autoclave in two consecutive portions. A cumulative TON of 2750 in less than 10 h was obtained. It is to be foreseen that an even higher TON can be reached, since no serious catalyst deactivation occurred over the two runs.

The unexpected high activity of the $RuCl_3$–phen system may be explained by the role the chloride anion plays in preventing the ligand redistribution reaction shown in eqn. (4). Its strong coordination may prevent extensive formation of inactive bis- and tris-phenanthroline complexes, thereby increasing the

Table 1 Synthesis of butanone from butadiene, catalysed by *in situ* generated ruthenium complexes[a]

Entry	Catalyst precursor[b]	TOF/h^{-1}[c]	k/h^{-1}[d]
1	—	0	0
2	$RuCl_3$	2.5[e]	N.d.[f]
3	$Ru(acac)_3$ + 1 eq. phen	230	0.11
4	$RuCl_3$ + 1 eq. phen	960	0.67
5	$RuCl_3$ + 2 eq. phen	230	0.19
6	$RuCl_3$ + 1 eq. bpy	250	0.22
7	$RuCl_3$ + 1 eq. phen + 3 eq. AgOTs	34[e]	0.64
8	$RuCl_3$ + 1 eq. phen[g]	700	0.41

[a] Reactions were performed in a 250 ml Hastelloy C autoclave at 145 °C for 10 h. Substrate: 10 ml butadiene. Acid: 3.5 mmol toluene-*p*-sulfonic acid (HOTs). Solvent: diglyme–water 70 : 30. [b] 0.09 mmol of metal complex was mixed *in situ* with the appropriate amount of ligand. [c] Initial turn over frequency (TOF) calculated with first order rate equations. Turnovers are determined with GLC. Selectivity to butanone: >95%. [d] Determined by fitting first order curves to autoclave pressure *vs.* time plots. [e] Average value over 10 h. [f] N.d. = not determined. [g] Acid: 1.75 mmol HCl

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concentration of catalytically active mono-phenanthroline ruthenium complexes. To verify this hypothesis, several samples taken during the reaction were analysed with mass spectrometry (MS). In the early stages of the reaction, Ru(III)- and Ru(II)-complexes with one phenanthroline, such as $[Ru(phen)Cl_2]^+$ and $[Ru(phen)(S)Cl]^+$ are dominant. This is the first time that ruthenium complexes containing only one phenanthroline ligand could be identified in this reaction.[6] Two other species are present in minor amounts: $[Ru(phen)_2Cl_2]^+$ and its Ru(II) analogue. Most noteworthy is the complete absence of complexes with three phenanthroline ligands. During the reaction, mono-phenanthroline complexes are converted to complexes with two phenanthroline ligands, but *not* with three. At the end of the 10 h reaction, complexes with only one phenanthroline ligand can still be detected. These results from MS prove that chloride ions indeed coordinate strongly to the ruthenium centre and prevent the formation of $[Ru(phen)_3]^{n+}$. In the $Ru(acac)_3$–phen system, between 20 and 40% of the ruthenium was present as $[Ru(phen)_3]^{2+}$.[6]

The present $RuCl_3$–phen system is much more sensitive to the ligand to metal ratio than the $Ru(acac)_3$–phen system. When two equivalents of phenanthroline are added to $RuCl_3$, the strong chloride coordination becomes a problem. $[Ru(phen)_2Cl_2]^+$ is formed instantly and chloride dissociation is slow.[9] With $Ru(acac)_3$, initial dissociation of acac is rate limiting and the influence of phenanthroline concentration is therefore much smaller.

The greater basicity and flexibility of bipyridine compared to phenanthroline render its coordination more reversible and this in turn makes ligand redistribution more prominent. Hence, the lower activity of $RuCl_3$ with one equivalent bpy can be explained by the increased formation of $[Ru(bpy)_2Cl_2]^+$, which is confirmed with MS on a spent catalyst.

Complete removal of chloride ions by silver(I) salts, replacing them with the non-coordinating anions toluene-*p*-sulfonate or trifluoromethane sulfonate, makes the catalyst much less stable. After an induction period, the reaction starts with a comparable rate ($k = 0.64\ h^{-1}$; Table 1, entry 7), but a TON of only 340 is reached after 10 h. These results underline the role of the chloride ion. Removal of chlorides increases ligand redistribution considerably, thereby reducing catalyst lifetime and overall product yield. On the other hand, increasing the chloride concentration by addition of NaCl or using HCl instead of toluene-*p*-sulfonic acid (Table 1, entry 8), decreases reaction rate and TON only slightly. This evidently shows that the hitherto found low activity of $RuCl_3$–phen systems was due to the amount of ligand and not to the presence of coordinating chloride anions.

In conclusion, an improved catalyst system has been found for direct synthesis of butanone from butadiene. $RuCl_3$ *in situ* combined with one equivalent of phenanthroline catalyses this conversion with an initial TOF of 960 h^{-1} and a cumulative TON of at least 2750 after 10 h. This superior result compared to previously reported systems emphasises the need for catalysts that prevent ligand redistribution. The possible use of relatively cheap $RuCl_3$ and HCl brings an industrial process for the direct synthesis of butanone from butadiene within reach. Future studies are aimed at further minimising ligand redistribution, optimisation of the reaction conditions as well as addressing the intriguing question on the valency of Ru in the active complex under butadiene hydration conditions and better understanding of deactivation reactions.

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Notes and references

† In a typical experiment, a high-pressure autoclave was filled with 0.09 mmol $[RuCl_3{\cdot}xH_2O]$, the appropriate amount of ligand and 3.5 mmol acid (for the acid-catalysed hydration of butadiene as shown in eqn. (2)). After addition of the diglyme–water (70:30) solvent mixture, the autoclave was closed and purged three times with dinitrogen. Next, buta-1,3-diene was added (10 ml) and the autoclave was heated to 145 °C. After 10 h, the autoclave was cooled to room temperature and the contents were analysed with GLC.

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