# First microwave synthesis of multiple metal-metal bond paddlewheel compounds†

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**A green and efficient microwave assisted synthesis of elusive tetrakis(diaryltriazenido)diruthenium(II) complexes was carried out under microwave irradiation. It is a simple, clean, and fast method that proceeds with good yield, in contrast with the poor ones reported in previous syntheses.**

## Introduction

Paddlewheel diruthenium complexes are a well known type of compounds with interesting properties.[1] Many species with O,O-donor bridging ligands, such as carboxylate or hydroxypyridinate, have been reported.[1,2] Complexes with N,N-donor ligands (anilinopyridinate, aminopyridinate, formamidinate, *etc.*) are also common in the literature, although their preparation usually involves some difficulties.[2] Among the N,N-ligand derivatives, triazenido complexes are especially scarce, even though the 1,3-diaryltriazenide species has been known and used for many years.[3] Moreover, the reported triazenido compounds have exceptional properties; for more than ten years, the only examples of low spin $Ru_2^{5+}$ complexes were tetrakis(diaryltriazenido) derivatives.[3a,4] One of the main reasons for this lack of tetrakis(triazenido)dimetal paddlewheel complexes could be the complexity of the synthesis of this type of compound.

In particular, tetrakis(triazenido)diruthenium(II) compounds had been previously synthesised by tedious multistep methods.[5] Such methods involved long reaction times, several extraction steps, low temperatures in some steps, and closed systems with inert atmosphere (see Scheme 1). The reagents and solvents used were often toxic and dangerous to handle (like BuLi). In this multistep reaction the final yield was not high, unlike the amount of generated residues. More recently, a new method for the preparation of the related chloridotetrakis(diphenyltriazenido)diruthenium complex using 2-methoxyethanol as a solvent was described,[6] but it required 48 hours of heating and only a 12% yield was reached.

To overcome the problems encountered in the previously reported methods, we thought that microwave irradiation could be helpful. Although barely used to prepare coordination complexes, microwave methods are well known to promote the synthesis of numerous organic compounds.[7] They usually lead to higher reaction rates and selectivity, high yield, improved purity, and need milder reaction conditions than other activation methods.

In this communication, we describe a novel, simple, clean, and fast microwave assisted method for the preparation of tetrakis(1,3-diaryltriazenido)diruthenium(II) compounds.

## Results and discussion

Two tetrakis(diaryltriazenido)diruthenium compounds have been obtained by the novel one-step microwave assisted method: tetrakis(1,3-diphenyltriazenido)diruthenium(II), compound **1**; and the new species tetrakis[1,3-di(*p*-fluorophenyl)-triazenido]diruthenium(II), compound **2**. The reactions were carried out with ethanol as a solvent. In this method, the initial $Ru_2^{5+}$ complex is reduced to the $Ru_2^{4+}$ compound. No additional reduction agent has been added to the reaction mixture, and therefore, ethanol is the most probable reducing agent. The nature of the final products has been unequivocally verified with the crystal structure determination of both complexes. A view of the structure of compound **2** is shown in Fig. 1.

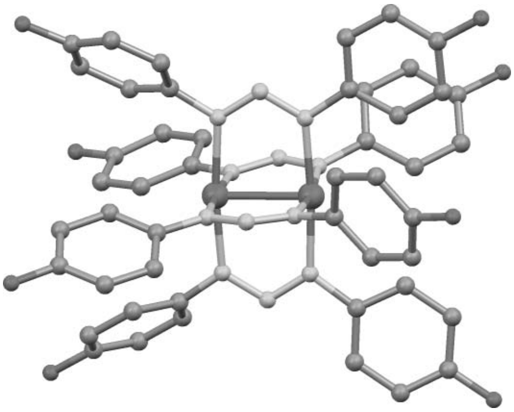

**Fig. 1** Molecular plot of compound **2** $[Ru_2(C_{12}N_3H_8F_2)_4]$. Hydrogen atoms have been omitted for clarity.

To optimise the reaction method, different parameters involved in the microwave assisted reactions that could affect the formation of the desired product were tested. Firstly, the initial microwave reaction conditions chosen were similar to the ones previously used in the conventional synthetic method reported by our group.[6] Thus, the reaction was carried out in 2-methoxyethanol, using the same reactants and ratio, and a temperature close to the boiling point of the solvent (130 °C) although the attempted reaction time, 8 hours, was shortened in

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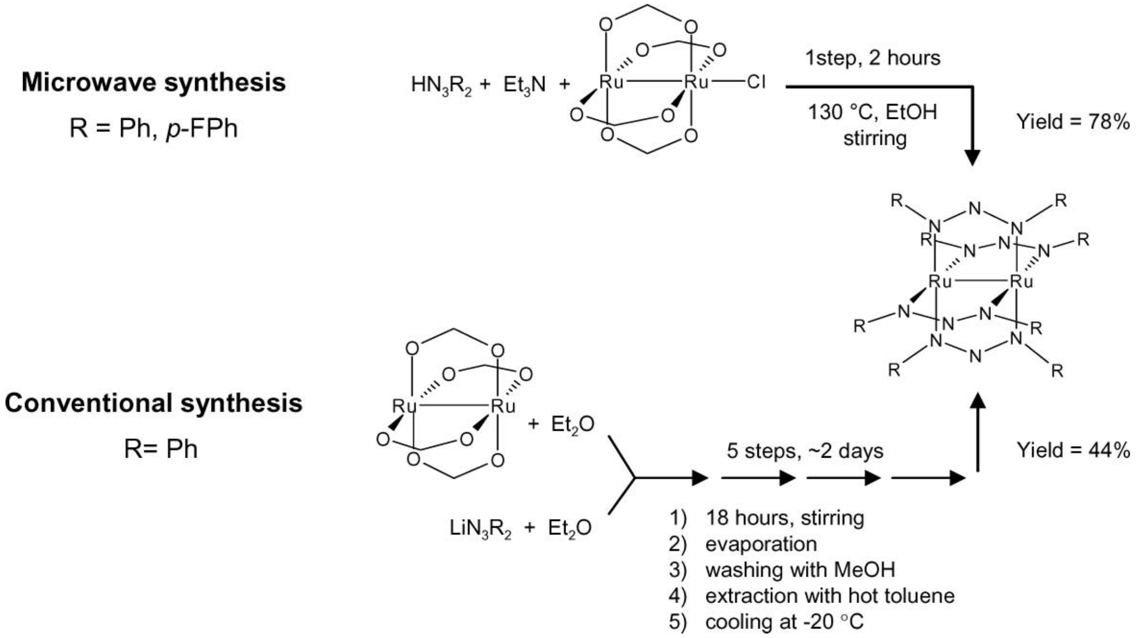

**Scheme 1** Procedure schemes from microwave and conventional synthesis.

comparison with the conventional method. The procedure was not successful with these reaction conditions.

Secondly, the solvent was changed to THF instead of 2-methoxyethanol, and the resulting product was a mixture of chloridotetrakis(diaryltriazenido)diruthenium(II,III) and tetrakis(diaryltriazenido)diruthenium(II) complexes. The nature of both complexes was established by elemental analysis, IR spectra and single crystal X-ray diffraction methods. All obtained data are in accordance with the results described in the literature[5,6] for these complexes. The effect of the reaction time was then explored, using both longer and shorter ones, with a similar result in every case: a mixture of the diruthenium(II) and diruthenium (II,III) species appeared.

The following step was the replacement of THF for a greener solvent, and the microwave assisted synthesis was attempted using ethanol as a solvent. The reaction in ethanol gave rise to the desired compound as a single phase in microcrystalline form. In this case, the reaction time has a crucial role in both the amount and the purity of the product obtained: the longer the reaction time, the better the yield, with a best result of 90% at 8 hours, although a reaction time as short as 2 hours leads to a 78% yield. It was also found that the $Ru_2$(II) compound was formed even with reaction times of 15 minutes. However, when the reaction was carried out for periods shorter than 2 hours, the final product was a mixture of both chloridotetrakis(diaryltriazenido)diruthenium(II,III) and tetrakis(diaryltriazenido)diruthenium(II) species, as also happened with THF as the solvent. Reaction times longer than 8 hours did not improve the amount of product obtained.

One of the principles of green chemistry applies to the maximization of atom economy. In the reaction mixture there were two reagents that could apparently be removed, as they did not take part in the final product: LiCl and $Et_3N$. The removal of LiCl from the reaction mixture was successfully attempted with identical results to the ones obtained in the reactions carried out with this reactant, regardless of the reaction time. However, $Et_3N$ proved essential for obtaining the desired product, as it is needed to deprotonate the ligand.

Other studied parameters were the dilution and the cooling time, and it was found that these factors modified only the crystallinity of the obtained phase and did not have any effect on the yield or the purity of the product.

The microwave assisted synthetic method described here has many advantages compared to the reaction procedure previously used (Scheme 1). Among them, the difference in the amount of solvent needed (20 times higher in the conventional method) and the total reaction time to obtain the final product are especially remarkable. With these results, we believe that microwave irradiation could be useful not only in obtaining paddlewheel compounds with triazenide ligands, but also in the synthesis of paddlewheel complexes with other N,N-donor ligands.

## Experimental

1,3-Diphenyltriazene, 1,3-di(*p*-fluorophenyl)triazene and chloridotetrakis(acetato)diruthenium(II,III) were synthesised by the methods reported in the literature.[8,9]

Microwave reactions were carried out in a ETHOS ONE microwave oven. The best yield was obtained with the following conditions: 0.25 mmol (0.12 g) of chloridotetrakis(acetato)diruthenium(II,III), 1.5 mmol triazene (0.25 g of 1,3-diphenyltriazene or 0.35 g for 1,3-di(*p*-fluorophenyl)triazene), 0.25 mL triethylamine and 10 mL absolute ethanol were added to a 85 mL TFM Teflon vessel with a magnetic stirrer. The vessel is sealed with a lid equipped with a temperature sensor and placed in the microwave oven. The reaction mixture is heated for 8 hours at 130 °C. The reaction mixture was left to cool afterwards, giving rise to the compound as a single phase of deep purple crystals with a 90% yield. The crystals were filtered off and washed with 10 mL of cold ethanol.

Compound **1** was characterised by IR spectra, elemental analyses and single crystal X ray diffraction, and the experimental data agreed with the literature.[5,6] Compound **2** was also characterised by the same methods.[10]

## Conclusions

The microwave irradiation of an ethanol solution of chloridotetrakis(acetato)diruthenium(II,III), diaryltriazene and triethylamine has proven to be an effective and selective method to prepare tetrakis(triazenido)diruthenium(II) compounds. This new method is much more sustainable and leads to higher yields than the previously published one, and it could facilitate the access to a family of compounds with interesting redox properties. Moreover, this procedure could be applied to improve the availability of other paddlewheel compounds with different bridging ligands. We are currently exploring this field with promising preliminary results.[11]

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10 Elemental Analyses for **2** $[Ru_2(C_{12}N_3H_8F_2)_4]$: experimental C, 50.98%; H, 3.01%; N, 14.48%, calculated C, 50.98%; H, 2.85%; N, 14.86%. IR/cm$^{-1}$ 3078, 3004, 1596, 1492, 1312, 1294, 1282, 1217, 1202, 1192, 1148, 1092, 1009, 884, 828, 811, 797, 720, 708, 667. X-ray structural analyses: Data for single crystals of compound **2** were collected on a Bruker SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (Mo-Kα radiation = 0.71073 Å). Data were collected over a hemisphere of the reciprocal space by a combination of three sets of exposures. Unit-cell dimensions were determined by a least-squares fit of all reflections collected. The compound crystallises in the monoclinic system, space group $P2_1/c$, with $a = 9.6596(4)$, $b = 38.896(2)$, and $c = 12.5248(5)$ Å, and $\beta = 102.989(1)°$. The, structure was solved by the Patterson method. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms. Calculations were carried out by using the SMART program for data collection and data reduction, and SHELX for refinement, with a final *R* factor of 0.0459 and a Goodness of Fit of 1.012. CCDC 766373 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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