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Combining sustainable synthesis of a versatile ruthenium dihydride complex with structure determination using group theory and spectroscopy

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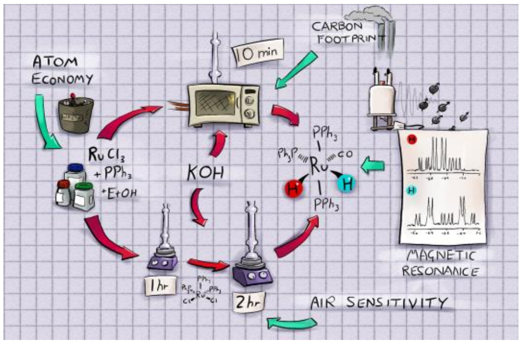
ABSTRACT

A good-yielding, two-step synthesis of $RuH_2(CO)(PPh_3)_3$ using conventional or microwave-assisted reflux techniques is described for use in undergraduate teaching laboratories. $RuH_2(CO)(PPh_3)_3$ is synthesised from $RuCl_3{\cdot}xH_2O$, PPh_3 and KOH in ethanol in two steps under an inert atmosphere or using a one-pot microwave-assisted reflux to reduce the reaction time to approximately 10 minutes. This makes this useful compound readily available within an undergraduate laboratory session via efficient and sustainable syntheses, enabling learning outcomes associated with air sensitive synthesis and application of group theory and spectroscopy to structure determination.

GRAPHICAL ABSTRACT



KEYWORDS

Upper-Division Undergraduate, Inorganic Chemistry, Laboratory Instruction, Hands-on Learning, Group Theory, IR Spectroscopy, NMR Spectroscopy, Synthesis, Green Chemistry

INTRODUCTION

Ruthenium complexes with hydride or carbonyl ligands are of significant interest in organometallic chemistry because of their role as catalysts in a variety of reactions.[1] Dihydridocarbonyltris(triphenylphosphine)ruthenium(II), $RuH_2(CO)(PPh_3)_3$ **1** (figure 1), is one example which can be synthesised in an undergraduate teaching laboratory.[2] It is an excellent candidate for illustrating multinuclear NMR coupling due to it's complex but very clear hydride spectrum and splitting patterns (figure 2).[2,3]

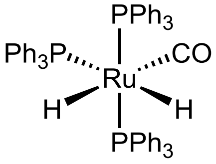


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Figure 1. The molecular structure of $RuH_2(CO)(PPh_3)_3$ **1**.

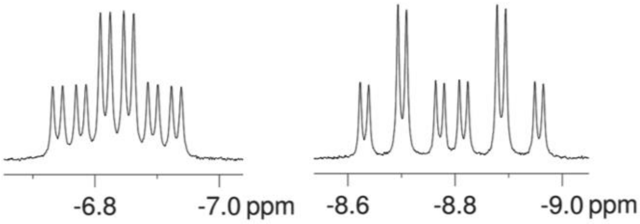


Figure 2. The ^{1}H-NMR peaks for the hydride atoms of **1** recorded at 400 MHz in $CDCl_3$ solution.[4]

Although yields of >70% have been reported for **1** in the established synthetic methods in the literature[2,5] our students typically achieved yields of around 18% by following these. We were able to improve typical yields slightly (to 35%) with a filtration step through alumina using large volumes of dichloromethane. Detailed analysis of the reaction mechanism by Samouei and Grushin has established that ethanol can replace formaldehyde as the source of the CO ligand in addition to acting as the hydride source and the reaction solvent.[3] Their synthesis is a much greener alternative because the principal solvent is ethanol and also because no purification steps are needed as **1** is the sole product precipitated from the reaction. They briefly outline a two-step synthesis, but do not explore it in detail.

In this paper, we report a robust adaptation of the two-step method suitable for the time limitations of an undergraduate laboratory experiment, and describe additional observations that are useful for its adoption. We also report a more time-efficient variant using microwave-assisted reflux, and we outline how group theory and spectroscopy can be applied to determine the structure of the complex.

EXPERIMENTAL PROCEDURE

Two-step synthesis of $RuH_2(CO)(PPh_3)_3$

$RuCl_3 \cdot xH_2O$ (0.08 g, 0.3 mmol) is dissolved in ethanol (20 cm^3) and added to a solution of PPh_3 (0.35 g, 13 mmol) in warm (30-40 °C) ethanol (20 cm^3). The reaction is heated to reflux under a nitrogen atmosphere for one hour. After cooling, the solution is filtered and the solid product washed (2 x 5 cm^3 ethanol) to give $RuCl_2(PPh_3)_3$ as dark-coloured micro crystals.

Ethanol (30 cm^3) and KOH (4 mol equivalents) are added to the $RuCl_2(PPh_3)_3$ and the mixture heated to reflux for two hours under nitrogen. Formation of a pale-coloured precipitate is observed. The reaction is cooled, the solution is filtered and the solid product washed successively with cold ethanol (2 x 5 cm^3), cold water (5 cm^3), cold ethanol (2 x 5 cm^3) and diethyl ether (1 cm^3), and dried thoroughly to give $RuH_2(CO)(PPh_3)_3$ as a pale-coloured solid. $\upsilon_{\mathrm{max/cm}}{}^{-1}$ (nujol mull) 1962w (RuH), 1942s (CO) and 1902w (RuH). ^{31}P-{^1H} NMR ($CDCl_3$, 25 °C) δ57.0 (2P, *d*, 18 Hz (*P*$Ph_3)_2$), 44.6 (1P, *t*, 20 Hz *P*Ph_3); ^1H-NMR ($CDCl_3$, 25 °C) δ −6.83 (1H, *tdd*, 31 Hz, 15 Hz, 6 Hz, OC-Ru-*H*), −8.80 (1H, *dtd*, 74 Hz, 28 Hz, 6 Hz, Ph_3P-Ru-*H*).

Microwave synthesis of $RuH_2(CO)(PPh_3)_3$

$RuCl_3.xH_2O$ (0.04 g, 0.15 mmol) and PPh_3 (0.3 g, 1.1 mmol) are added to ethanol (50 cm^3) and nitrogen gas bubbled steadily through the solution for five minutes. The nitrogen is removed and the solution warmed in the microwave for one minute before adding four pellets of KOH. The mixture is heated to reflux in the microwave for five periods of two minutes (ten minutes total irradiation time). During this time, the solution lightens in colour and a light precipitate is formed. The mixture is cooled, filtered, and the solid product washed successively with cold ethanol (2 x 5 cm^3), cold water (5 cm^3), cold ethanol (2 x 5 cm^3), and diethyl ether (1 cm^3), and dried thoroughly to give $RuH_2(CO)(PPh_3)_3$ as a pale-coloured solid.

HAZARDS

PPh_3 is an irritant, $RuCl_3.xH_2O$ and KOH cause severe burns, and both ruthenium-containing products are harmful. Gloves should be worn to handle them. $RuCl_3.xH_2O$ and KOH are hygroscopic and will form corrosive sludges if spilled. They should be kept contained and spillages cleared up quickly. All manipulations should be carried out in a fume hood.

Adapting a domestic microwave[6] can compromise the internal radiation shielding and radiation testing should be done before work commences to establish a safe working perimeter. Ethanol absorbs microwave radiation very efficiently. Extremely vigorous reflux is achieved in less than one minute of full power irradiation of the cold solvent and within seconds when the solvent is hot. Our solution is to extend the reflux control system[6] water hose with additional coils around the flask inside the microwave chamber. Further details are provided in the supporting information. It is recommended that students try the microwave setup with pure ethanol in order to familiarise themselves with the procedure before they add their reagents.

DISCUSSION

Specific Learning Outcomes

The synthesis of **1** has the benefit that it is based on work described in the recent literature.[3] It also has great versatility in terms of specific learning outcomes as follows:

1) As an example of a compound with metal-carbonyl and metal-hydrogen bonds and applications in catalysis.
2) To illustrate the use of ethanol as a green solvent, giving students an appreciation of the wider environmental impact of laboratory work.
3) As a test of ability in performing an air-sensitive reaction.
4) To provide a practical application of theoretical points made in group theory and NMR spectroscopy lectures.
5) To illustrate how chemical structure can be determined by combining several analysis techniques.

Our specific learning objective on the practical side is for students to successfully perform a reaction at reflux under nitrogen atmosphere. The two-step synthesis is ideal for this because the first step is only moderately sensitive to oxygen so experience can be gained before attempting the more sensitive second step. If students are unable to exclude air from their reaction, the second step does not work and a penalty is applied in the assessment. Successful achievement of this outcome is demonstrated by the presence of **1** in the IR and NMR spectra.

Our specific learning outcome on the theory side is that students relate IR and NMR spectroscopic properties to structure. To do this, students follow the scientific method to eliminate possible structural isomers based on the spectroscopic evidence gathered. The work supports learning of group theory by requiring its use in analysing the ν(RuH) absorptions in the IR spectrum, and it supports the NMR spectroscopy courses through the analysis of the coupling constants in the spectra. Assessment of this outcome gauges success at each step and credit is also given for the level of professionalism (*i.e.* thoroughness) demonstrated in assigning and interpreting spectra.

Two-step synthesis

The synthesis of **1** is reported as a longer-duration one-pot reaction and as two shorter steps.[3] The two-step synthesis fits nicely into our laboratory schedule and has the additional benefit that a student gains skill and confidence through setting up the equipment twice. Typical student yields of **1** are of the order of 57%.

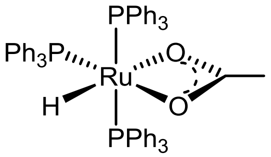
The first step, the synthesis of $RuCl_2(PPh_3)_3$, works well and is reliable, which is consistent with Linn's assertion that it is easily prepared.[7] Test reactions performed without an inert atmosphere showed no decrease in yield, however, our undergraduates perform this step under N_2 for practice.

Where the second step, the synthesis of **1**, is successful, the dark-coloured reaction mixture lightens and a pale precipitate forms within 15-20 minutes. This step is very sensitive to changes in reaction conditions consistent with the complex chemistry disguised by the apparent simplicity of the reaction equation,[3,8] and product appearance can vary dramatically from off-white to shades of pink, purple, brown or grey.

Where the reaction mixture remains dark brown or grey, the precipitate is often dark grey in colour. The identity of the dark-coloured impurity is unknown, however, it is insoluble in deuterochloroform and is removed by filtration through alumina so a good quality NMR spectrum of **1** can still be obtained.

The reaction mixture can also adopt either of two different red colours. A scarlet red appears to be consistent with the formation of an acetate complex $RuH(OAc)(PPh_3)_3$ **2** (figure 3). This complex is highly soluble in ethanol and is a reported byproduct of reaction where water is present, or where there is limited KOH or ethanol.[3] The scarlet colour does not prevent formation of **1** and it is removed by filtration leaving **1** in good purity and yield. However, we have observed evidence of acetic acid in the IR spectrum on occasion.

A burgundy red colour is often followed by formation of the monohydride complex, $RuCl(H)(CO)(PPh_3)_3$ **3** (figure 3). This is easily identifiable in the IR (nujol mull, υ_{RuH} 2015m and υ_{CO} 1924vs, 1905m cm^{-1}) and sometimes in the NMR (δ_H −7.1 *br dt*) although it reacts with $CDCl_3$ to give a black precipitate and the peaks in the room-temperature spectrum are poorly resolved. Comparing reported syntheses of **1** and **3**[2] suggests that formation of **3** can be attributed to insufficient KOH. We have found that reactions can be "saved" by addition of more KOH in the early stages of reflux immediately either red colour is observed.



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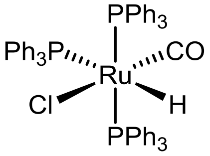

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Figure 3. The molecular structures of alternative products $RuH(OAc)(PPh_3)_3$ **2** and $RuCl(H)(CO)(PPh_3)_3$ **3**.

The second step is also sensitive to the presence of nitrogen gas. The literature uses argon as the inert atmosphere[3,7] presumably because a possible intermediate, $Ru(H_2)(H)_2(PPh_3)_3$, is known to react with N_2 to give a dinitrogen complex.[8,9] Where a very high N_2 flow is maintained during reaction or where N_2 is passed through the reflux, an N_2 complex is observed with a characteristic υ(NN) at 2147 cm^{-1} in the IR spectrum. However, we find that the N_2 complex does not form if the reflux is vigorous and a gentle flow of N_2 is used as a blanket over the top of the reaction.

Microwave synthesis

Heating reactions to reflux on a hot plate has a significant environmental impact. A 750 W hot plate operating for approximately three hours consumes 2.25 kWh of electricity producing roughly 1.13 kg of CO_2 (based on the carbon footprint of average

UK grid electricity). If a reaction is reduced to approximately ten minutes, a microwave consuming 1.3 kW should produce only 0.1 kg of CO_2.

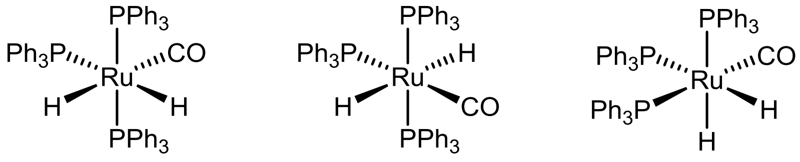
The synthesis of **1** can be done in a one-pot method using a microwave-assisted reflux technique.[6] Trial runs with volunteers resulted in typical product yields of 55% and average yields when this method was used in a lab class were 45%. The efficacy of microwave heating overcomes the retardation effect of PPh_3 on the reaction[3] and negates the filtration step needed in the two-step synthesis to remove excess PPh_3. Performing the reaction without the initial N_2 degassing step results in a lower yield and also gives quantities of insoluble black material. We have also found that giving the PPh_3 time to dissolve and react with the $RuCl_3{\cdot}xH_2O$ before adding KOH is key to the success of this reaction and that warming the solution before the addition is beneficial to the yield. Combining all three reagents in cold ethanol before heating results in the formation of insoluble black material and no detectable quantity of **1**.

We have observed that **1** will slowly precipitate out of the filtered microwave-reaction solution if left to stand for a period of time. It is unclear whether this is because the reaction is incomplete. However, it is known that **1** undergoes intramolecular ligand exchange[10] and so it could be that this fluxionality is enabling a kinetic product to form **1** as the thermodynamic product which is insoluble in the reaction medium.

Structural determination

The synthesis of **1** has three possible product isomers not including enantiomers (figure 4). Students beginning with the formula of the compound, $Ru(CO)H_2(PPh_3)_3$, can proceed to identify these, and can use molecular modeling kits if desired to gain practice at working with structures in three dimensions. Novice students may draw the same isomer in different orientations but this confusion can be resolved by asking them to describe the positions of ligands in terms of *cis*, *trans*, *mer* and *fac* relationships.

From here, students predict the spectroscopic properties they would expect to see for each isomer and compare their predictions with the spectroscopic evidence.



mer-cis *mer-trans* *fac*

Figure 4. The three possible isomers of **1**.

Provided the nujol mull is well-ground, the IR spectrum of **1** shows two Ru-H peaks either side of the strong ν(CO). Analysing the RuH stretches of the possible isomers using group theory principles, rules out the *mer-trans* isomer because the symmetric stretch does not have an associated dipole change and would not be seen in the IR. Analysis of the ^{31}P-{^{1}H} NMR spectrum allows a good estimation of product purity, and gives practice in identifying environments and measuring coupling constants. However, ^{31}P-{^{1}H} NMR does not eliminate any isomers because they each have two phosphorus environments. Analysis of the Ru-H peaks in the ^{1}H-NMR spectrum reveals that the product is the *mer-cis* isomer. The hydrides in the *fac* isomer are in the same chemical environment and would give a different coupling pattern. Taking the students through the analysis in this way also reinforces the point that the number of chemical environments is a poor indicator of the number of peaks visible in an IR spectrum.

CONCLUSIONS

$RuH_2(CO)(PPh_3)_3$ is a useful teaching compound because its spectroscopic properties enable discussion of group theory principles in relation to infrared spectroscopy and its NMR spectroscopic properties are a clear demonstration of multi-nuclear coupling. A new greener synthesis can be used to introduce students to air sensitive reactions. This synthesis has been successfully applied in an undergraduate teaching lab and an understanding of the complexity of the reaction mixture helps ensure a robust and reliable experiment. A microwave variant has also been shown to work, with careful control of reflux leading to the rapid formation of product and a significant reduction in the carbon footprint of the reaction.

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

Student instructions, laboratory teacher notes, and the list of questions used in the structural analysis are included in the supporting information along with information about the course in Sheffield, greater detail about the implementation of the syntheses, a summary of the chemistry related to the synthesis, and typical IR and NMR spectra of **1**. This material is available free of charge at http://pubs.acs.org.

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