



A fast and easy approach to the synthesis of Zeise's salt using microwave heating

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ARTICLE INFO

Article history:

Received 10 February 2009

Accepted 11 February 2009

Available online 27 February 2009

Keywords:

Microwave

Platinum

Zeise's salt

Alkene complex

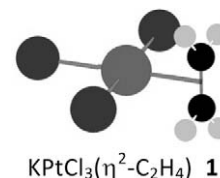
ABSTRACT

A fast and easy approach to the synthesis of Zeise's salt, $\text{KPtCl}_3(\text{C}_2\text{H}_4)$, is reported using microwave heating. The reaction is complete after 15 min at 130 °C using K_2PtCl_4 as starting material, a 1:1:1 ratio of water:ethanol:concentrated HCl as solvent, and a loading of 50 psi of ethene.

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Zeise's salt, trichloro(ethylene)-platinate(II) **1**, is credited as the first organometallic compound to be isolated in essentially pure form [1,2]. The synthesis and study of this, and the related dimeric compound *trans*-di- μ -chlorodichloro-bis(ethylene)diplatinum(II) **2** played a considerable role in the development of bonding theory in both inorganic and organic chemistry [3,4]. It is probable that Zeise first prepared **1** by first boiling platinum (IV) chloride in ethanol and then treating this solution with potassium chloride [5]. For a long while after its discovery, modifications of the procedure for making **1** all generally required prolonged reaction times (7–14 days) or else the use of high pressures [6]. More recently a method has been developed which utilizes tin (II) chloride as a catalyst for the reaction between ethene and potassium hexachloroplatinate [7]. The reaction can be performed in a few hours at atmospheric pressure. The use of a tin catalyst, as well as being somewhat undesirable, can lead to problems in product isolation. The applications of Zeise's salt in catalysis [8] and as a precursor for functional materials [9] as well as its proving a versatile starting material for synthesis of organometallics [10] sparked our interest in developing a fast, easy route for its preparation using microwave heating. Interestingly, while organic chemists have used microwave heating extensively [11], there have been relatively few reports of its use in preparative organometallic chemistry [12]. Using scientific microwave apparatus it is possible to perform reactions either in sealed vessels or open reflux arrangements. Using a custom-built gas-loading accessory for introduction of carbon monoxide or hydrogen into a reaction vessel we have recently reported the synthesis of $\text{Ru}_3(\text{CO})_{12}$ from RuCl_3 as well as $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ from $\text{Ru}_3(\text{CO})_{12}$ and $\text{H}_2\text{Os}_3(\text{CO})_{10}$ from $\text{Os}_3(\text{CO})_{12}$

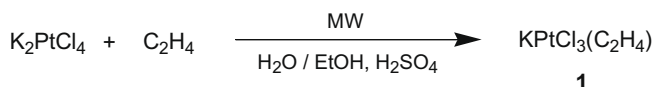
[13]. We believed that by extending this approach we could prepare Zeise's salt using ethene as a gaseous reagent.



As an initial set of reaction conditions we chose to use K_2PtCl_4 (**3**) as starting metal salt and dilute hydrochloric acid as the solvent. Working on the 50 mg scale of **3** and loading with 50 psi (3.45 bar) of ethene in a 10 mL capacity sealed tube, we heated the reaction mixture to 130 °C and held it at this temperature for 15 min [14]. This yielded a slightly yellow solution but with significant plating of platinum metal on the inner surface of the reaction tube. This is undesirable since, in the presence of a microwave field, metal films heat very rapidly and can lead to the melting of glass tubes which, if under pressure, can fail. We attributed the deposition of platinum, at least in part, to the limited solubility of **3** in dilute hydrochloric acid. Thus, we repeated the reaction using more concentrated acid. A 1:1 mix of water to concentrated HCl (v:v) proved to be more suitable, **3** being totally soluble. Upon heating under a pressure of ethene, an orange solution was formed but with significantly less metal deposition. Analysis of the solution showed that very little **3** had reacted. Ethene is poorly soluble in water so we believed that by modifying the solvent we could facilitate the reaction. Thus, we decided to trial ethanol as a co-solvent since this would increase the solubility of ethene in the reaction mixture. A 1:1:1 (v:v:v) ratio of water to concentrated

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Scheme 1. Fifty psi ethene, heat to 130 °C and hold until a total time of 15 min has elapsed.

hydrochloric acid to ethanol proved to be successful and, after 15 min at 130 °C we obtained a clear yellow solution, analysis of which showed that **1** was present in significant quantities (Scheme 1).

Our next objective was to find an easy way to obtain **1** in pure form so we could reliably quantify our results. Filtration to remove any metallic platinum formed during the course of the reaction followed by removal of the ethanol/water solvent mixture under reduced pressure led to a yellow solid. Not unexpectedly, this contained KCl, the byproduct formed during the reaction. To remove this we took advantage of the fact that while **1** is readily soluble in acetone, KCl is not. Thus, simply adding acetone to the crude solid product mixture allowed for separation of the two components. Using this approach we were able to isolate **1** in pure form by filtration to remove the KCl followed by evaporation of the acetone under reduced pressure. Using this method we were able to isolate **1** in 89% yield.

In many cases, reactions performed using microwave heating can reach completion in very short times. To determine if 15 min was the optimum time for the preparation of **1**, we repeated the reaction but held it at 130 °C for just 5 min. We obtained a 60% yield of **1** showing that, while the reaction is well advanced within 5 min, to reach completion a longer reaction time is required. Extending the time beyond 15 min had no significant impact on product yield.

Our final objective was to test the scalability of the protocol. Moving first to using 100 mg of **3**, we performed the reaction in a larger 80 mL capacity sealed tube. We kept all conditions the same (a 1:1:1 ratio of water:conc. HCl:ethanol as solvent, 50 psi ethene, 130 °C for 15 min) and obtained an identical product yield after purification [15]. Scaling the reaction to the 0.5 g level was also successful, an 87% yield of **1** being obtained.

In summary, we have developed a fast and easy approach to the synthesis of Zeise's salt using microwave heating. The reaction is complete after 15 min at 130 °C using K_2PtCl_4 as starting material, a 1:1:1 ratio of water: concentrated HCl: ethanol as solvent and 50 psi of ethene.

Acknowledgement

We thank the University of Connecticut and the American Chemical Society Petroleum Research Foundation (45433-AC1) for funding.

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- [14] Reactions were performed using a CEM Discover microwave unit. This consists of a continuous focused microwave power delivery system with operator selectable power output from 0 to 300 W. Reactions were performed either in 10 mL or 80 mL capacity sealed tubes. The temperature of the contents of the vessel was monitored using an IR sensor located underneath the reaction vessel or a fiber-optic temperature probe inserted directly into the reaction mixture. Pressure was controlled by a load cell connected directly to the vessel. The contents of the reaction vessel are stirred by means of an electromagnet located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel. Temperature, pressure and power profiles were monitored using commercially available software provided by the microwave manufacturer. For loading reaction vessels with gas, either a commercially available gas-loading interface or an in-house built interface was used.
- [15] Synthesis of $[\text{KPtCl}_3(\text{C}_2\text{H}_4)]$: To a dry 80-mL glass vessel equipped with a magnetic stirbar was added a solution of K_2PtCl_4 (100 mg, 0.241 mmol) in a mixture of water (5 mL), ethanol (5 mL) and concentrated hydrochloric acid (5 mL). The vessel was sealed in the microwave apparatus, with a septum containing ports for pressure and temperature measurement devices. A pressure of 50 psi ethene was introduced into the vessel, the pressure sensor being kept closed. The line to the carbon monoxide regulator was then closed and the pressure vented to the atmosphere through the pressure sensor. This process was repeated two more times, then the vessel loaded to 50 psi with ethene and sealed. With stirring, the reaction mixture was heated to 130 °C using an initial microwave power of 300 W and held at this temperature until a total time of 15 min had elapsed. The reaction mixture was then cooled to 50 °C, at which time the remaining pressure was carefully vented. The contents of the reaction vessel were transferred into a round bottom flask and the solvent removed on a rotary evaporator. Acetone (5 mL) was added to the flask to extract $\text{KPtCl}_3(\text{C}_2\text{H}_4)$. This was repeated two times, and the combined acetone washings cooled to approximately 0 °C and filtered. Removal of the solvent left pure $\text{KPtCl}_3(\text{C}_2\text{H}_4)$ in 89% yield (79 mg). ^1H NMR (400 MHz, d_6 -acetone, δ in ppm): 4.21 ($^1\text{J Pt} = 64$ Hz). ^{13}C NMR (100 MHz, d_6 -acetone, δ in ppm): 66.0 ($^1\text{J Pt} = 195$ Hz).