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Microwave Assisted Synthesis of Chloropentahaptocyclopentadienediphenylphosphinoethaneruthenium(II)

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Running Title: Synthesis of Chloropentahaptocyclopentadienediphenylphosphinoethaneruthenium(II)

Microwave-assisted syntheses have been implemented in the preparation of both organic and inorganic compounds. Advantages include increased yields and faster reaction times (Kingston and Haswell 1997). In ruthenium chemistry, Greene and Mingos first used microwave technology to prepare a series of Ru(II)-bipyridine complexes in the early 90's (Greene and Mingos 1991). Several polypyridine complexes have since been prepared using microwaves (Matsumura-Inoue et al. 1994, Anderson et al. 2006). The $Ru(dmso)_4Cl_2$ complex has been synthesized using open vessel (Sun et al. 2010) and closed vessel (Harvey et al. 2009) reactions. Other examples of microwave-assisted syntheses include the preparation of ruthenium-thiosemicarbazone complexes (Beckford et al. 2009) and ruthenium-tris(pyrazolyl)borate sandwich complexes (Zagermann et al. 2011).

A useful starting material for the preparation of new ruthenium-containing complexes is CpRu(dppe)Cl. Chloride substitution reactions have resulted in the formation of compounds of general form CpRu(dppe)L, where L = polyalkynes (Bruce et al. 2012), carbenes (Bowie et al. 2012), P_4 (Di Vaira et al. 2006), carborane (Basato et al. 2007), thiol (Treichel et al. 1991, Shaw et al. 2007), thiolate (Shaw et al. 2007, Shawakfeh et al. 2008) and stannic halides (de Moura et al. 2003) to name a few.

The CpRu(dppe)Cl compound is synthesized by refluxing $CpRu(PPh_3)_2Cl$ and 1,2-bis(diphenyl-phosphino)ethane in benzene, followed by reduction of volume and subsequent precipitation of the product by a 4/1 ethyl ether/hexane mixture (Ashby et al. 1979). This reaction involves a reflux of 8 hours and an additional 10 hours for precipitating the final product. Reduction in volume is also critical, as too little reduction leads to reduced yields. The length of reaction time and the difficulties in preparing this product have led us to explore the use of microwave irradiation for improving the preparation of CpRu(dppe)Cl.

Microwave-assisted synthesis of CpRu(dppe)Cl was performed using a CEM Discover microwave reactor. Solvents were obtained from Fisher Scientific and were used as received without further purification. ACS-grade chloroform-*d* stored over molecular sieves was used as a solvent for NMR. ^{1}H NMR of the products was carried out using a Bruker Topspin 300-MHz NMR. A Buchi rotary evaporator was used for concentrating the reaction mixtures. The starting material, $CpRu(PPh_3)_2Cl$, was prepared as described in the literature (Ashby et al. 1979) for comparison of the two reactions.

For the microwave reaction, 0.050g (0.069 mmol) of $CpRu(PPh_3)_2Cl$ and 0.027g (0.069 mmol) of 1,2-bis(diphenylphosphino)ethane were dissolved in 2 mL of toluene in a reaction tube. A stir bar was added, nitrogen gas was bubbled into the tubes for one minute before setting them in the microwave reactor. Once the reaction was completed, the reaction mixtures were transferred into a 50-mL round-bottom flask and were concentrated using a rotary evaporator until the reaction-mixture volume was approximately 1mL. To the round-bottom flask, 25 mL of 4/1 ethyl ether/hexane mixture was added and was allowed to cool to 0 ^{o}C overnight. The yellow precipitate that formed overnight was filtered. To the filtrate, approximately 13 mL of hexane was added. Orange precipitate that formed was filtered and washed with 4/1 ethyl ether/hexane mixture and dried. Yield = 32 %. Product was characterized by ^{1}H NMR. (δ, CDCl3, ppm: 7.3, 7.9, m, 20H, phenyl groups; 4.55, s, 5H, C_5H_5; 2.5, m, 4H, -CH_2-).

In order to study the effect of reaction parameters on product yield, reaction parameters such as hold time, ramp time and temperature was varied. In a typical reaction involving change in hold time, reactions were performed for 5 minutes, 6 minutes, 7 minutes and 8 minutes. Temperature was kept constant at 95 ^{o}C for all the reactions. Results from these reactions are shown in Table 1.

A second set of reactions was performed by varying the temperature of the microwave reactor.

Reactions were performed at 95, 85, 80 and 70 °C. The hold time was kept constant at 5 minutes. Results from these reactions are shown in Table 2. For the last two trials with a reaction temperature of either 80 or 70 °C, pure product was not obtained; therefore, no yield was reported.

Table 1: Reaction parameters and yields from hold time trials

Hold time (min)	T (°C)	Ramp time (min)	Actual yield (g)	% yield
5	95	10	0.012	30
6	95	12	0.004	10
7	95	14	0.006	20
8	95	16	0.008	20

Table 2: Reaction parameters and yields from temperature trials

T (°C)	Hold time (min)	Ramp time (min)	Actual yield (g)	% yield
95	5	10	0.013	32.
85	5	10	0.009	20
80	5	10	No yield	No yield
70	5	10	No yield	No yield

The last set of reactions was performed by varying the ramp time. Reactions were performed for 7 minutes, 8 minutes, 9 minutes and 10 minutes. The hold time was kept constant at 5 minutes, and the temperature was maintained at 95 °C. Results from these reactions are shown in Table 3.

From the trials performed by varying reaction parameters, the reaction performed for a ramp time of 8 minutes and a hold time of 5 minutes at 95 °C gave the highest yield (38%). Setup time for microwave reactions is 10 minutes, and the reactions take as long as 5-10 minutes for each tube, so overall time for the reaction is 15-20 minutes for each reaction tube. It was noticed that yields from multiple reaction tubes ranged from a low of 2.5% to a maximum of 37%, which

Table 3: Reaction parameters and yields from ramp time trials

Ramp time (min)	T (°C)	Hold time (min)	Actual yield (g)	% yield
10	95	5	0.012	30
9	95	5	0.009	20
8	95	5	0.015	38
7	95	5	0.006	20

meant that several tubes had to be prepared to get the required gram amounts necessary for further reactions. By comparison, the set up time for the reaction using conventional heating is less than 10 minutes, but involves a longer reaction time (15-16 hours). The yield obtained from this reaction (80 %, Ashby et al. 1979) is approximately equal to yields obtained from 5 microwave reaction tubes combined.

Better yields are achieved by conventional heating compared to our microwave synthesis. The microwave synthesis results in a decrease in reaction time. Thus, if time is a factor, microwave synthesis is a better method for synthesizing CpRu(dppe)Cl, whereas if higher yields are required, conventional heating is a better method for synthesizing CpRu(dppe)Cl.

In conclusion, microwave-assisted synthesis can be utilized for the preparation of CpRu(dppe)Cl, but the poor yields and difficulty in purifying the reaction product makes the conventional literature preparation (Ashby et al. 1979) the preferred synthetic technique for the preparation of CpRu(dppe)Cl.

Acknowledgments

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