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Microwave-Assisted Synthesis of Metal Complexes

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Abstract: Microwave heating has received considerable attention as a powerful synthetic tool for metal complexes in many fields of inorganic chemistry and material science. Since the 1990s, numerous metal complexes have been synthesized using the microwave technique. However, only a few studies have discussed such synthesis. In this review, we focus on microwave-assisted synthesis of metal complexes. We discuss the background to microwave chemistry in metal complex synthesis, the use of domestic microwave ovens for both closed- and open-system reactions, and some useful microwave heating techniques. In addition, we present a summary of reaction schemes from selected publications published in the past two decades.

Keywords: Coordination compound, metal complex, microwave heating, organometallic compound, synthesis, transition metal.

1. INTRODUCTION

The fundamentals of microwave chemistry were studied and reported in the post-war era for applications such as decomposing simple organic compounds in a microwave discharge, drying inorganic salts, and wet ashing techniques of biological and organic materials [1-5]. The first two studies of organic synthesis by means of the microwave heating technique were reported by Geyde *et al.* and Giguere *et al.* in 1986 [6, 7]. These reports focused on the significant rate acceleration for reactions; microwave heating reactions are still attracting the attention of synthetic chemists. Microwave irradiation results in dielectric heating, which is different from classical thermal heating. Nowadays, the basic principles and theory of dielectric heating, the characteristic "superheating effect," and the experimental results, *i.e.*, considerably shortened reaction time, are widely studied and are known features of microwave-assisted synthesis [8-11].

Microwave heating is warming caused by rotations and vibrations of substances when the charged particles and dipoles in a substance interact with the electromagnetic field of the microwave. The microwave frequency region ranges from 0.3 to 30 GHz (1 cm^{-1} m), although these days domestic microwave ovens usually operate at 2.45 GHz. Since other frequency ranges are widely used for radars and telecommunications, the remaining available frequencies of 2.45 GHz and 0.9 GHz are used to prevent jamming. Thus, the constituents of an electromagnetic field around the forced sphere in a substance rapidly change directions as fast as 2.45×10^9/s, and therefore, microwave irradiation results in rapid heating. For this reason, microwave heating is different from classical thermal heating and is capable of causing selective, homogeneous, and rapid heating. With these intriguing features of microwave chemistry, many efforts have been made, particularly in organic synthesis, and more than 20 years have passed since the first report on microwave-assisted synthesis. However, a considerably less number of reports appear to have been focused on metal complex synthesis than on microwave synthesis. In this review, we focus on the microwave-assisted synthesis of metal complexes. Instrumentations, useful examples of the applications of microwave synthesis, and a list of reaction schemes are summarized. Metal complexes obtained by microwave reactions were first reported by Baghurst *et al.* in 1989 [12]. Some transient-metal sandwich compounds were synthesized by microwave irradiation in a closed system at high temperature and pressure. Ali *et al.* reported a ligand exchange reaction by microwave irradiation in the same year [13]. From then on, many efforts have been made to synthesize metal complexes by microwave irradiation.

Research topics and studies on metal complexes are increasing significantly, because of their attractive prospect of playing a key role in functional materials. Metal complexes as photosensitizers and photocatalysts in photofunctional materials are now contributing to providing solutions to energy and environmental issues [14, 15]. Coupling reactions and asymmetric syntheses are promoted by organometallic compounds [16, 17]. Organic light-emitting device materials, which are one of the most popular subjects in materials science in the first decade of the 21st century, and metal complexes are candidate materials for practical applications [18]. The applications for metal complexes are growing faster at an astonishing rate. At the same time, scientists are challenged to design and synthesize more intricate compounds than ever before. The microwave technique would be one of the most powerful tools in preparing these materials.

2. INSTRUMENTATION OF DOMESTIC MICROWAVE OVEN

There are two types of reaction systems for microwave-assisted synthesis. One is a closed system that is capable of running a reaction under high pressure and temperature; the other one is an open system in which a reaction is usually carried out by refluxing. The first microwave-assisted metal complex was obtained by the closed system reaction [12]. This reaction employed a Teflon vessel that can sustain a temperature of 250 °C and pressures of up to 80 atm; however, the apparatus was not equipped with any sensors to monitor temperature, microwave power, and pressure; therefore, the experiments were carried out with potential risks. In particular, since domestic microwave ovens were often used during the early days of microwave synthesis chemistry, it was apparently not easy to perform safe experiments. In this context, some important experiments were conducted during the 1990's using modified domestic microwave ovens and reported in several publications [19-23]. Fig. (**1**) shows a schematic view of the vessel used for a closed-system reaction [19]. The microwave oven was perforated on its top and the vessel, which is connected to a pressure gauge *via* a pipeline, was inserted through the hole. The reaction vessel is made of Pyrex and covered with a protective sheath. With this modification, microwave reactions in a closed system were performed safely by monitoring the pressure level during the reactions. Nowadays, microwave apparatuses equipped with pressure and thermo sensors are commercially available. Although the for-research devices are considerably more expensive than domestic microwave ovens, it is better to use the former for safety reasons.

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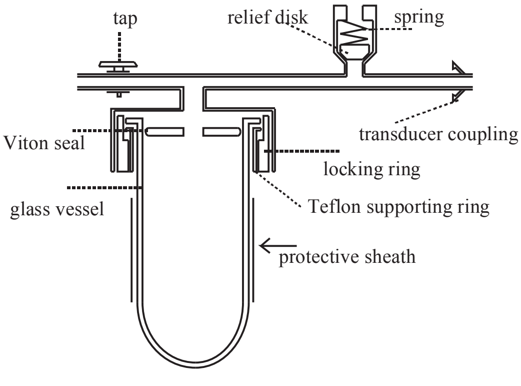


Fig. (1). Design of vessel for closed-system microwave reaction

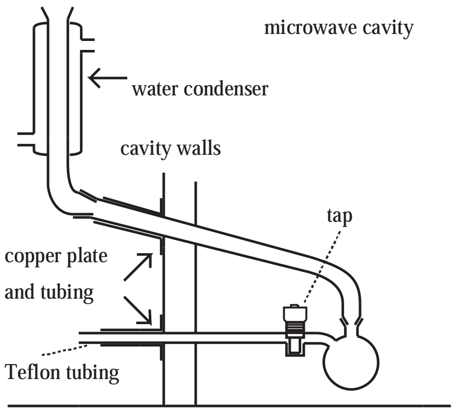


Fig. (2). Side-connected arrangement for open-system microwave reaction.

In contrast, open-system reactions are relatively safer than closed ones because the former reactions are usually carried out under atmospheric pressure. In addition, regular glass apparatuses, which are less expensive than high-pressure apparatuses, can be used for these reactions. However, a domestic microwave oven needs to be perforated to provide a connection between the inside and the outside of the microwave cavity. Water, which is the most popular coolant for the reflux condenser, effectively absorbs microwaves. The condenser should be located outside the microwave cavity and should be connected to the reaction vessel. Generally, domestic microwave ovens can be modified in two ways for the chemical reaction. Fig. (**2**) shows one of the two modifications, which is a side-connected arrangement [20]. The reaction flask is connected to an air-cooled tube and a water-cooled condenser through a hole in the sidewall. A second hole in the sidewall is used to attach a Teflon tube, which is connected to an inert gas supply, to maintain the reaction mixture under inert atmosphere. Copper plates and tubes are attached to both ports to prevent leakage of microwaves during reactions. Alternatively, Matsumura *et al.* developed a modified domestic microwave oven that has a vertically connected arrangement, as shown in Fig. (**3**) [21, 22]. In this modification, the microwave oven was perforated on the top to allow the connection of a reflux condenser. A flanged metal pipe was also attached in order to prevent leakage of the microwaves. A capillary tube connected to an inert gas supply is introduced through the condenser to bubble inert gas into the reaction solution. This setup has a simple arrangement, and its operation may be easy for microwave reactions. Ardon *et al.* reported a similar modified microwave oven, shown in Fig. (**4**) [23]. It has a supplementary reflux control system in addition to Matsumura's single reflux. A couple of side ports are used to fit a glass U-tube through which water is passed. Excess microwave radiation in the cavity is absorbed by the water in the U-tube, and this brings the reaction mixture to a moderate reflux.

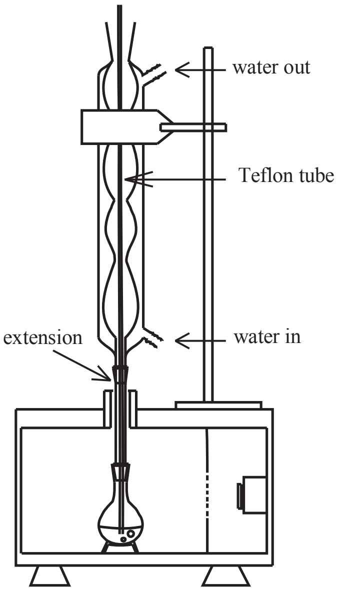


Fig. (3). Vertically connected arrangement for open-system microwave reaction.

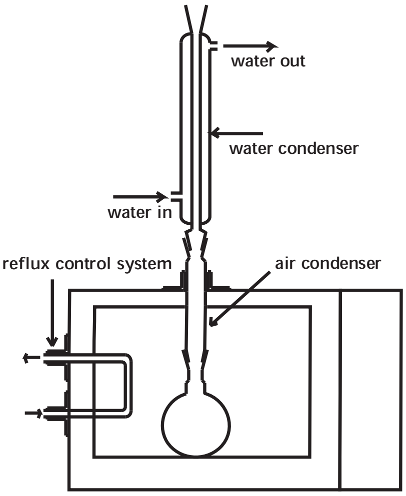
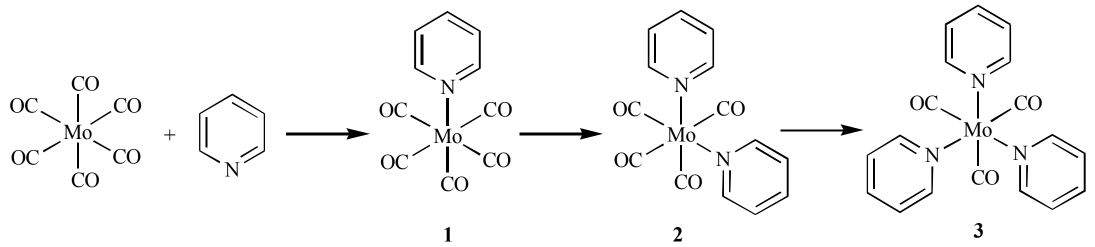


Fig. (4). Vertically connected arrangement for open-system microwave reaction with a reflux control system.

As described earlier in this section, inexpensive domestic microwave ovens can be easily modified to run chemical reactions in both closed and open systems; however, there are still some limitations in monitoring and controlling the microwave power, temperature, and pressure; therefore, the researcher needs to be careful to reduce the risks faced in carrying out a chemical reaction using the apparatus.

3. MICROWAVE-ASSISTED SYNTHESIS OF METAL COMPLEXES

The advantage of microwave synthesis is essentially that it significantly accelerates the rate of reactions. In general, the complexation reaction of a first row transition metal element is relatively fast. When this metal is replaced with a second row element, more vigorous conditions are required for the complexation reaction to afford the desired metal complex. Similarly, more vigorous conditions are required if a second row metal is replaced with a



Scheme 1.

third row element. For example, in the complexation reaction between the iron group metals and the bidentate ligand 2,2′-bipyridine (bpy),

$$M^{2+} + 3bpy \rightarrow [M(bpy)_3]^{2+} \text{ (M = Fe, Ru, or Os)}$$

the ligand immediately coordinates with iron(II) when these species are mixed together. However, in the case of ruthenium(II), the aqueous reaction mixture has to be refluxed for 30 min to obtain $[Ru(bpy)_3]^{2+}$ [24]. Moreover, the complexation of osmium(II) requires a solvent with a high boiling point, such as ethylene glycol, and the reaction mixture must be refluxed for approximately 1 h [25]. This example illustrates a relatively simple reaction; much more vigorous conditions and longer reaction times would be required in the synthesis of a coordination compound containing more complex ligands. In such reactions that require harsh conditions, microwave heating can play a key role, and many studies have focused on the preparation of metal complexes using the microwave technique. In fact, from the perspective of the periodic table, microwave-assisted reactions for second and/or third row metal complexes seem to predominate over those for first row elements. At present, numerous studies have been conducted on microwave synthesis of metal complexes [12, 13, 19, 21-23, 26-36, 40-110], and it may not be feasible to provide a comprehensive overview of these studies. In this section, the typical reactions that prominently feature in microwave synthesis are described, and many other reactions are listed in Tables **1**–**6**.

Group 6 Metal Complexes

Selected reaction schemes involving the microwave-assisted synthesis of group 6 metal complexes are summarized in Table **1**. Molybdenum is the most studied element among the group 6 metals in this field. Leadbeater *et al.* reported an apparatus for real-time monitoring of organometallic reactions under microwave irradiation using *in situ* Raman spectroscopy [28]. The ligand exchange reaction of $Mo(CO)_6$ was studied by the reactor system shown in Scheme **1**. A solution of $Mo(CO)_6$ in pyridine (py) was heated from room temperature to 180 °C over a period of 90 s using a microwave power of 150 W, and the Raman spectrum (2400–1550 cm^{-1}) was measured every 6 s. Four new bands at 2071 cm^{-1}, 1981 cm^{-1}, 1892 cm^{-1}, and 1600 cm^{-1} increased in intensity within 20 s of irradiation, while the peaks at ν_{CO} = 2119 cm^{-1} (E_g) and ν_{CO} = 2015 cm^{-1} (A_{1g}) decreased. By comparison with spectra from authentic samples, the new bands were attributed to $Mo(py)_n(CO)_{6-n}$ (**1**; n = 1, **2**; n = 2, **3**; n = 3). Maintaining the temperature of the reaction mixture at 180 °C for a further 1 min resulted in further conversion to **3**. This observation serves as good evidence of the fact that microwave heating can accelerate the reaction to completion within seconds, which is otherwise difficult to achieve by conventional heating.

Table 1. List of Microwave-Assisted Syntheses of Group 6 Metal Complexes

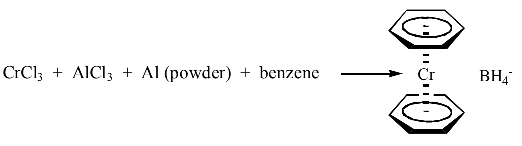
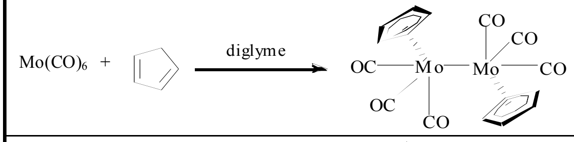
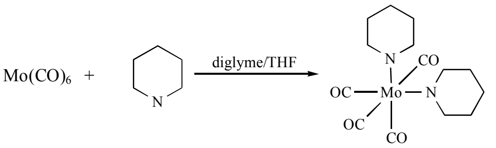
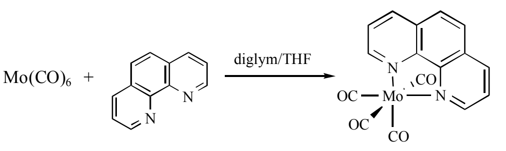
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Cr	*η*-arene complex	20–45 min, yields = 45–52% (3 examples)	[22]
	Mo	*η*-arene complex	20 min–4 h, yields = 18–94% (5 examples)	[27]
	Mo	N-coordinated complex	40 min, yield = 78% (1 example) in Ref. [23]; 15 min–2 h, 39–96% (15 examples) in Ref. [30]	[23], [27]
	Mo	N-coordinated complex	15 min–2 h, yields = 14–96% (20 examples)	[27]

Table 1. contd….

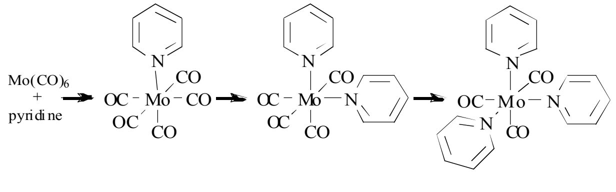
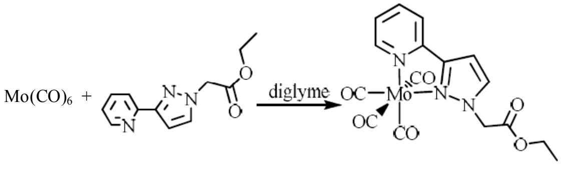
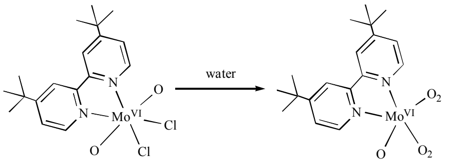
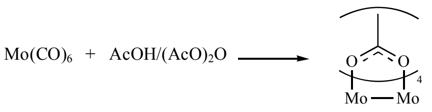
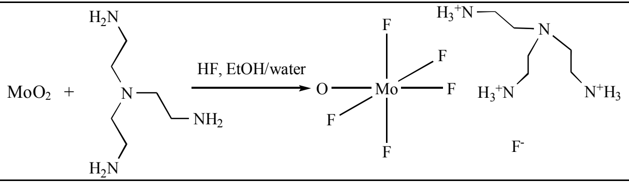
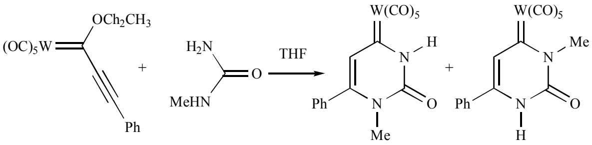
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Mo	N-coordinated complex	2.5 min (total), yields not given (3 examples)	[28]
	Mo	N-coordinated complex	30 s–15 min, yields = 63–85% (2 examples)	[29]
	Mo	N-coordinated complex	4 h, yield = 12% (1 example). This product can not be obtained from conventional heating.	[30]
	Mo	acetato complex	30 min, yield = 65% (1 example) in Ref. [19]; 45 min, 48% (1 example) in Ref. [27]	[19], [27]
	Mo	halogeno complex	1 h, yield not given (1 example)	[31]
	W	carbene complex	30 s–30 min, yields = 7–97% (15 examples).	[32]

Table 2. List of Microwave-Assisted Syntheses of Group 7 Metal Complexes

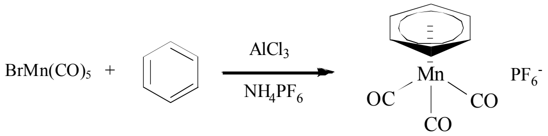
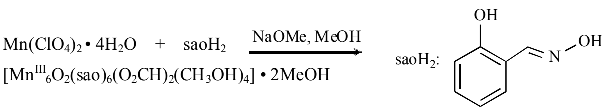
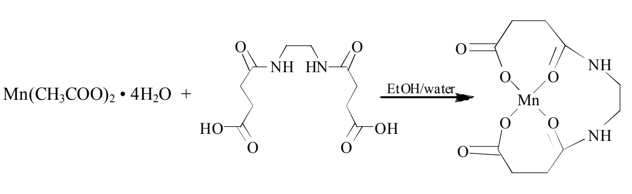
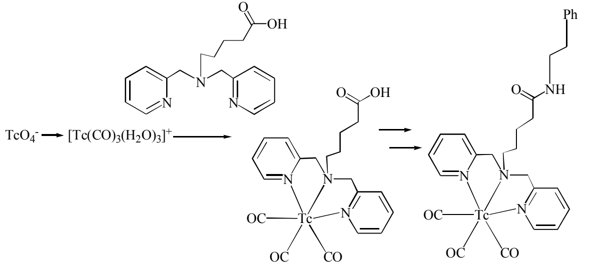
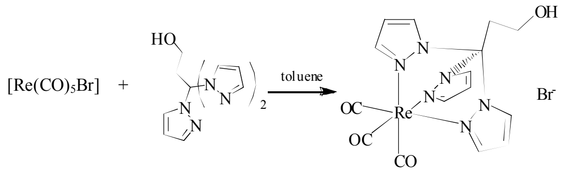
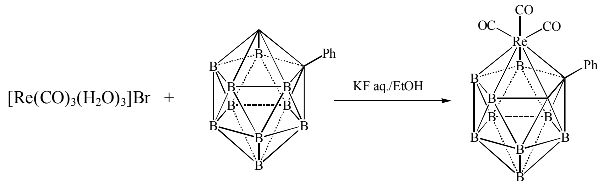
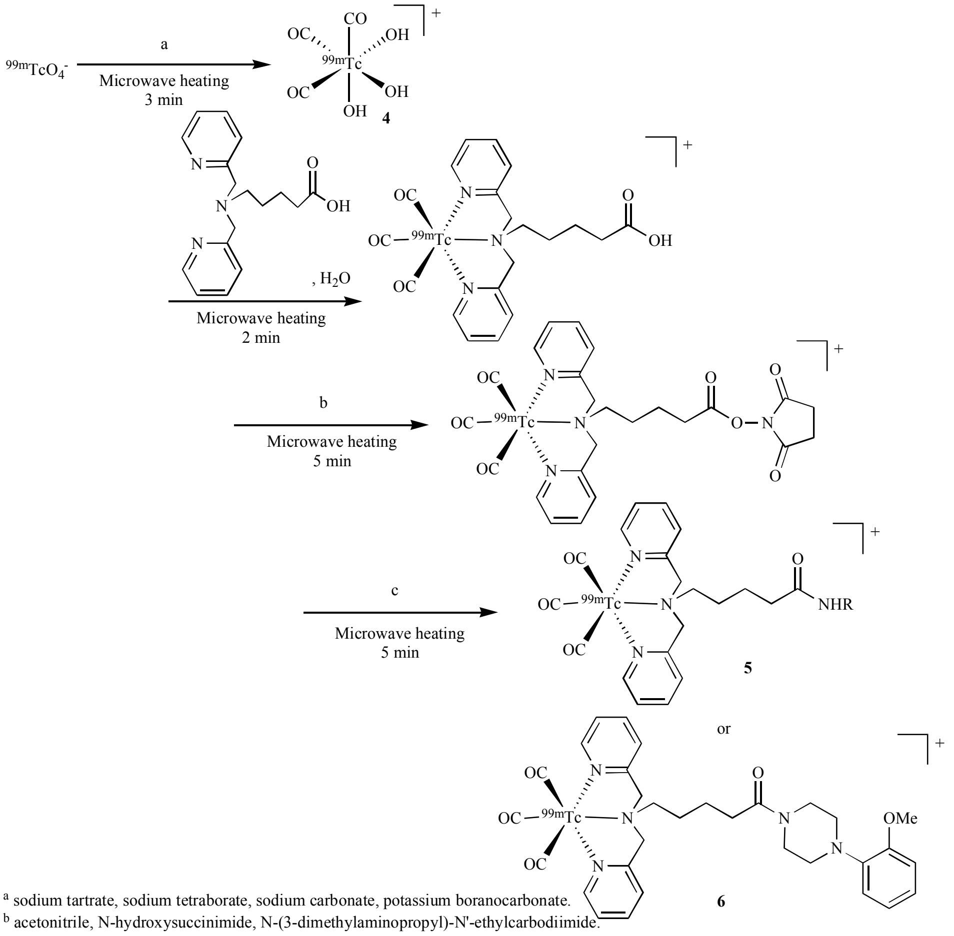
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Mn	η-arene complex	3 min, yields = 0–56% (9 examples)	[33]
	Mn	cluster complex	5 min, yield = 80% (1 example)	[34]
	Mn	tetradentated complex	1.5–4 min, yields = 25–65% (4 examples)	[35]

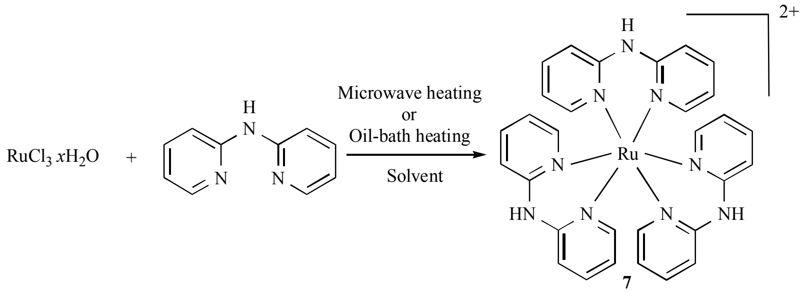
Table 2. contd…

Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Tc	N-coordinated complex	10–15 min (total), yields = 77–92% (9 examples)	[36]
	Re	N-coordinated complex	10 min × n (monitored by infrared spectroscopy), yields = 68–95% (3 examples)	[40]
	Re	metallocarbor-ane complex	5–15 min, yields = 63–90% (7 examples) in Ref. [41]; 15–60 min, yields = 57–94% (7 examples) in Ref. [42]	[41], [42]



[a] sodium tartrate, sodium tetraborate, sodium carbonate, potassium boranocarbonate.
[b] acetonitrile, N-hydroxysuccinimide, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide.
[c] acetonitrile, N,N-diethylethylenediamine, benzylamine, or 1-(2-methoxy)-phenylpiperazine.

Scheme 2.



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Entry	Solvent	Heating method	Reaction time (min)	Isolated yield (%)	Ref.
1	Ethylene glycol	Microwave heating	15	91	[21]
2	Water/Ethanol	Oil-bath heating	180	80	[38]
3	Ethylene glycol	Microwave heating	20	86	this work
4	Ethylene glycol	Oil-bath heating	20	42	this work

Scheme 3.

Group 7 Metal Complexes

Selected reaction schemes involving the microwave-assisted synthesis of group 7 metal complexes are summarized in Table **2**. Technetium, a synthetic element, does not have any stable isotopes and it would be difficult to store technetium-containing products over a large duration. Due to its rate acceleration effect in complexation reactions, microwave heating may be an important synthetic tool for short-lived group 7 isotopes, *e.g.*, ^{99m}Tc and $^{186/188}$Re. Causey *et al.* reported the efficient microwave synthesis of ^{99m}Tc complexes for use as radiopharmaceuticals in clinical studies [36]. Radioactive ^{99m}Tc has been widely used as a radioactive agent in positron emission tomography (PET) because of its favorable half life (6 h) and gamma ray energy (E_γ = 140 keV). Pre-treated prior to administration to patients, instant labeling kits consisting of a radionuclide, ligand(s), buffer, and reducing agent have been used for their low cost, convenience, and high reproducibility. The expedient synthesis of ^{99m}Tc(CO)$_3$-bifunctional chelate complexes is shown in Scheme **2**. The reaction starts with ^{99m}TcO$_4^-$ and carbonylation agents to initially yield **4**, followed by several steps to yield **5** or **6**. The radioactivity of each compound was characterized by γ-HPLC. Every reaction was carried out with microwave heating and the entire procedure was completed in less than 30 min with a decay-corrected yield of 86%. In contrast, conventional heating required a total of over 2 h, and decay-corrected yields were 57%. The approach described here represents a movement away from conventional instant kits toward automated multistep synthesis and purification platforms that should help to accelerate the process of discovering novel ^{99m}Tc agents for molecular imaging and therapy and increase the number of new targeted agents being used in clinical applications.

Group 8 Metal Complexes

Selected reaction schemes involving microwave-assisted synthesis of group 8 metal complexes are summarized in Table **3**. Ruthenium complexes are among the most studied group 8 metals as seen from Table **3**. The microwave effect in the preparation of a well-known tris-chelated ruthenium complex will be discussed in this section. Matsumura *et al.* reported that [Ru(Hdpa)$_3$]$^{2+}$ (**7**; Hdpa: 2,2′-dipyridylamine) can be synthesized within 20 min of microwave irradiation at yields as high as 91% from ruthenium(III) chloride and Hdpa (Scheme **3**) [21]. In contrast, a conventional method involving oil-bath heating gives **7** with a 30% yield for a reaction time of 2 h. The low yield in the latter case is due to the formation of impurities during the reaction. Togano *et al.* reported the synthesis of **7** using "ruthenium blue" solution [37], wherein the product was obtained by using ruthenium(III) chloride and aqueous ethanol, as the starting materials, with a yield of up to 80% [38]. We synthesized **7** by both microwave heating and oil-bath heating under the same reaction conditions [39] and determined the isolated yields of **7** to investigate the influence of the heating source. Microwave-assisted reaction afforded a crude product as a yellow powder with an initial yield of 94%, which was recrystallized by slow vapor diffusion of ether into an acetonitrile solution of the product to give yellow crystals with a yield of 86%. The slight decrease in the yield can be attributed to the absence of isolating processes, resulting in the near quantitative yield. On the other hand, a dark green solid was obtained with a yield of 95% by oil-bath heating under the same reaction conditions. The dark green color indicates that ruthenium(III) substances could not be removed even after repeated recrystallization. After purification by alumina column chromatography, the product afforded a bright yellow powder with a yield of 42%. The results of accelerated complexation and reduction of ruthenium ions by microwave irradiation showed that ionic metal salts and/or polar ligands were activated by microwave heating to form **7**. Microwave heating makes it possible to obtain the desired product in a shorter reaction time. Furthermore, the reaction yield improved possibly because of the prevention of undesirable reactant decomposition and the elimination of unnecessary side reactions.

Table 3. List of Microwave-Assisted Syntheses of Group 8 Metal Complexes

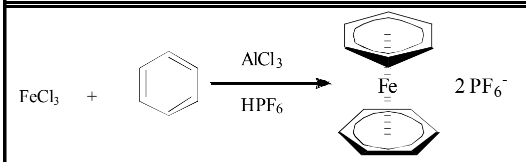
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Fe	η-arene complex	2 min, yields = 2–37% (9 examples)	[43]

Table 3. contd…

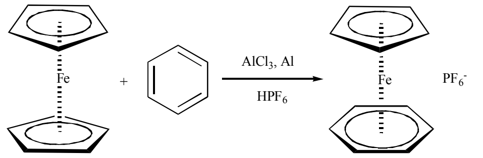
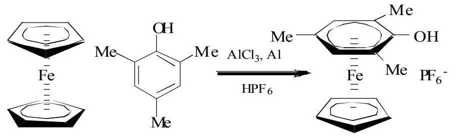
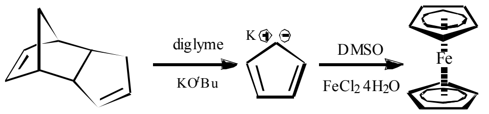
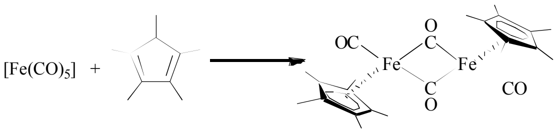
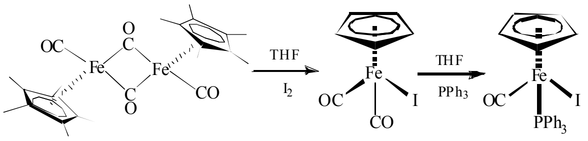
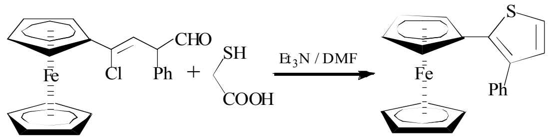
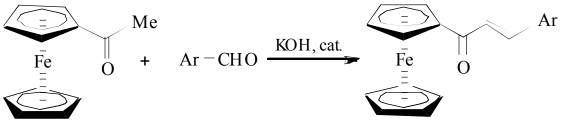
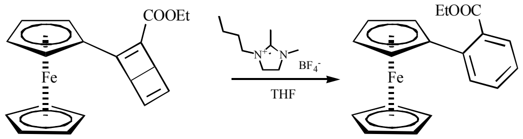
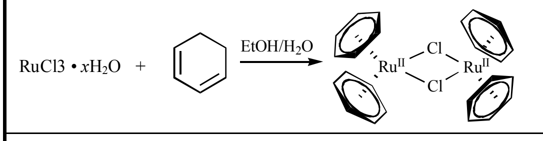
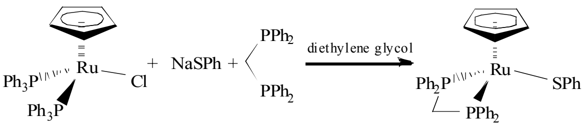
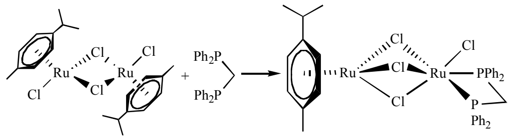
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Fe	η-arene complex	3–4 min, yields = 48–99% (9 examples)	[43]
	Fe	η-arene complex	3.5 min, yields = 9–95% (7 examples) in Ref. [36]; 2–8 min, 0–94% (46 examples) in Ref. [45]; 2–5 min, 5–55% (7 examples) in Ref. [46]	[33], [44], [45]
	Fe	η-arene complex	15 min (total), yield = 86% (1 example)	[46]
	Fe	η-arene complex	10 min, yield = 88% (1 example)	[46]
	Fe	η-arene complex	20 min (total), yields = 76–90% (3 examples)	[46]
	Fe	η-arene complex	0.5–7 min, yields = 15–94% (11 examples)	[47]
 cat.: Aliquat 336 as a phase transfer catalyst	Fe	η-arene complex	2–7 min, yields = 41–88% (6 examples)	[48]
	Fe	η-arene complex	6 h, yields = 76–80% (2 examples)	[49]
	Ru	η-arene complex	35–50s, yields = 68–91% (4 examples) in Ref. [12]; 0.5–9 min, 66–84% (2 examples) in Ref. [19]; 10–30 min, 67–87% (3 examples) in Ref. [50]	[12], [19], [50]
	Ru	η-arene complex	2 min, yields = 88–91% (5 examples)	[51]
	Ru	η-arene complex	5 min–5 h, yields = 60–94% (11 examples)	[52]

Table 3. contd…

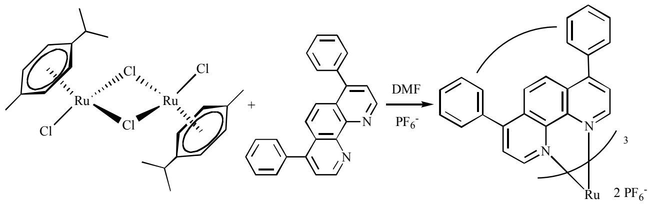
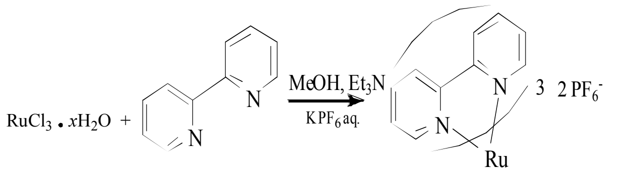
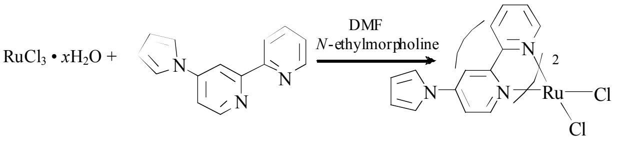
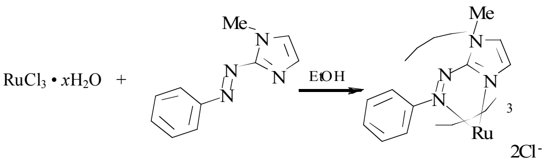
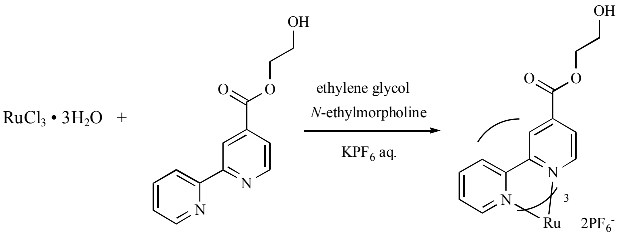
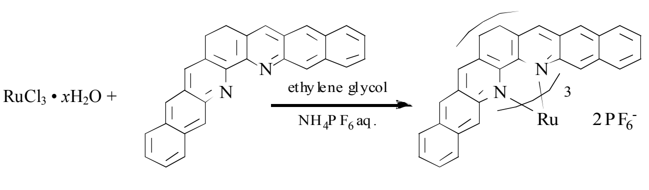
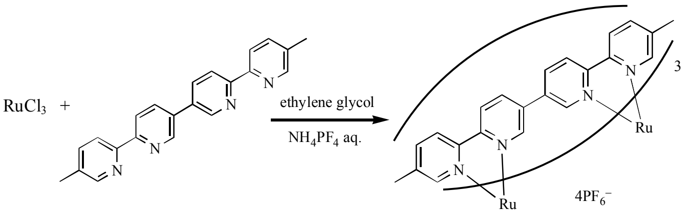
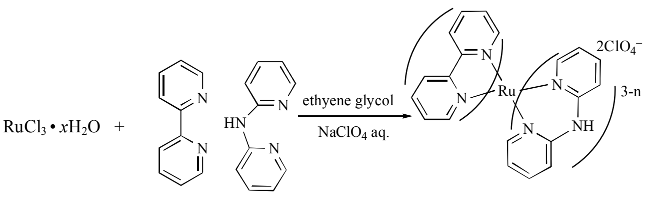
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Ru	N-coordinated complex	5 min, yield = 89% (1 example)	[53]
	Ru	N-coordinated complex	10 min, yields = 87% (1 example) in Ref. [19]; 20 min, 57–95% (10 examples) in Ref. [21]; 40 s, yields = 68–94% (4 examples) in Ref. [54]; 5 min, 88% (1 example) in Ref. [55]	[19], [21], [54], [55]
	Ru	N-coordinated complex	10 min, yields not given (4 examples)	[56]
	Ru	N-coordinated complex	30 min (total), yields = 55–70% (12 examples)	[57]
	Ru	N-coordinated complex	4 min, yields = 82% (3 examples)	[58]
	Ru	N-coordinated complex	15–30 min, yields = 15–44% (4 examples)	[59]
	Ru	N-coordinated complex	4.5 h, yield = 36% (1 example)	[60]
	Ru	N-coordinated complex	10 min, yields not given (47 examples)	[61]

Table 3. contd…

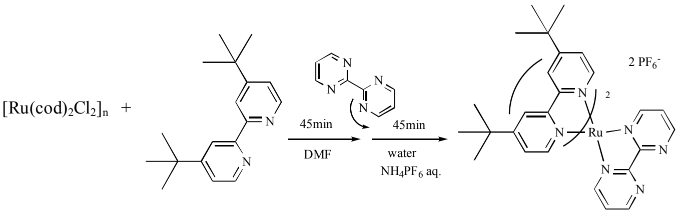
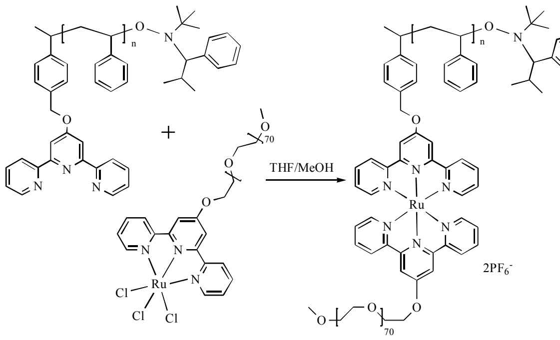
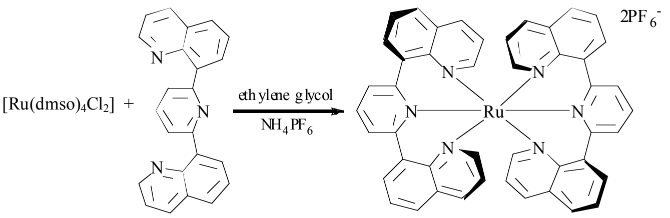
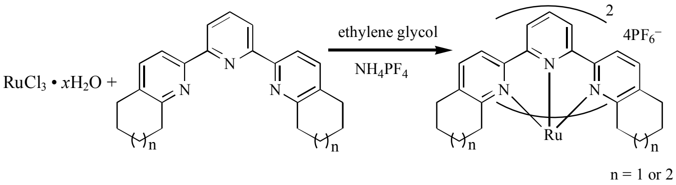
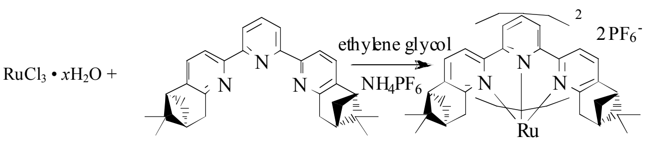
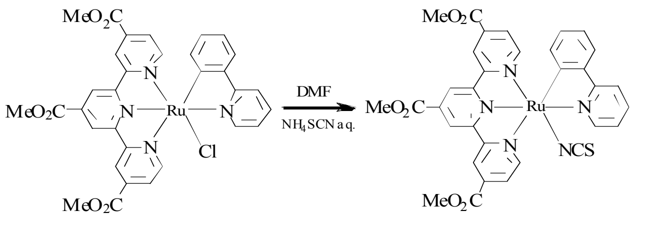
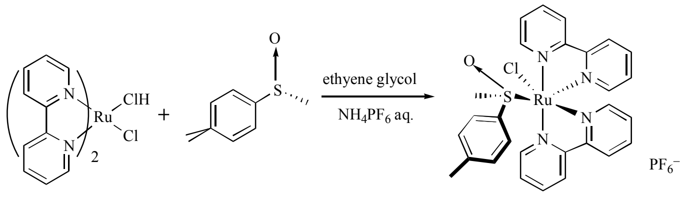
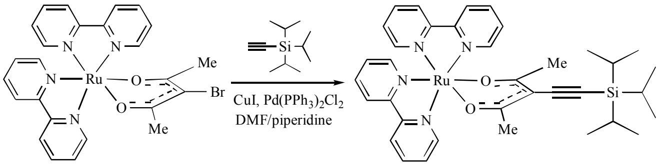
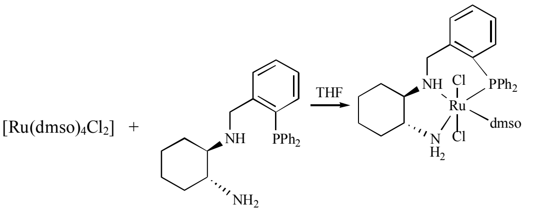
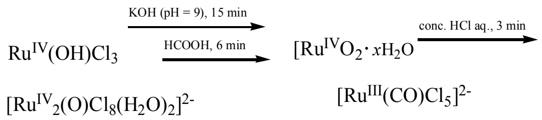
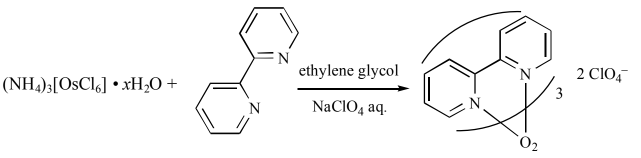
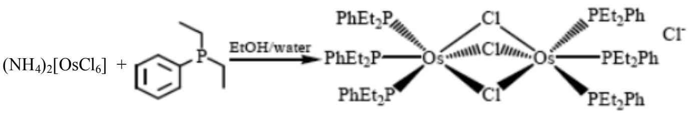
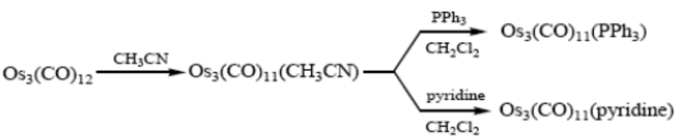
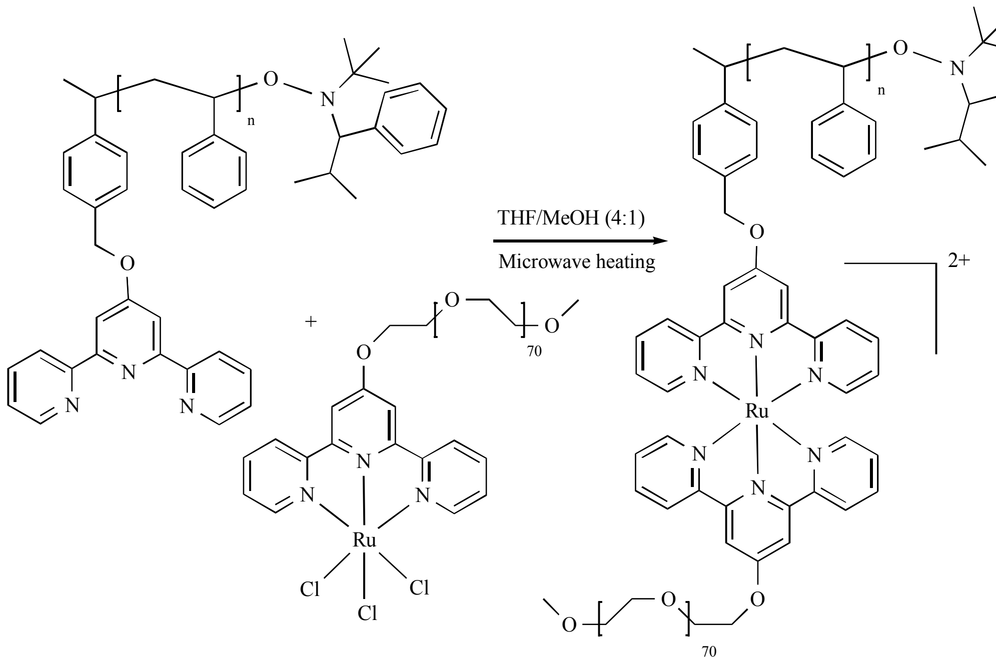
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Ru	N-coordinated complex	45–135 min (total), yields = 63–98% (6 examples) in Ref. [62]; 1 h, 90% (1 example) in Ref. [63]	[62], [63]
	Ru	N-coordinated complex	1 h, yields = 19–38% (3 examples)	[26]
	Ru	N-coordinated complex	20 min, yield = 87% (1 example) in Ref. [64]; 20 min, 22% (1 example) in Ref. [65]; 5 min, 12–64% (4 examples) in Ref. [66]	[64], [65], [66]
	Ru	N-coordinated complex	4 min, yields not given (2 examples)	[67]
	Ru	N-coordinated complex	4 min, yields = 89–99% (3 examples)	[68]
	Ru	N-coordinated complex	10 min, yields = 31–37% (2 examples)	[69]
	Ru	N-coordinated complex	2–4 min, yields = 70–97% (8 examples)	[70]

Table 3. contd…

Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Ru	N-coordinated complex	1 h, yield = 62% (1 example)	[71]
$RuCl_3·xH_2O + PPh_3 \longrightarrow RuCl_2(PPh_3)_3$	Ru	P-coordinated complex	30 min, yields = 85–94% (2 examples)	[50]
	Ru	P-coordinated complex	15 min, yield = 65% (1 example)	[72]
$K_4[Ru^{IV}{}_2OCl_{10}] \xrightarrow{EtOH/HCl\ aq.} K_2[Ru^{III}(H_2O)Cl_5]$	Ru	halogeno complex	2 min, yields not given (1 example)	[73]
 $Ru^{IV}(OH)Cl_3 \xrightarrow[HCOOH,\ 6\ min]{KOH\ (pH = 9),\ 15\ min} [Ru^{IV}O_2·xH_2O \xrightarrow{conc.\ HCl\ aq.,\ 3\ min}$ $[Ru^{IV}{}_2(O)Cl_8(H_2O)_2]^{2-}$ $[Ru^{III}(CO)Cl_5]^{2-}$	Ru	halogeno complex	24 min (total), yield not given (1 example)	[74]
$RuCl_3·xH_2O + CO \xrightarrow{CsCO_3,\ MeOH} Ru_3(CO)_{12}$	Ru	cluster complex	1–15 min, yields = 90–98% (5 examples)	[75]
	Os	N-coordinated complex	20 min, yields = 65–74% (2 examples)	[21]
	Os	P-coordinated complex	5 min, yields = 60% (4 examples)	[76]
	Os	cluster complex	5–7min, yields = 67–82% (3 examples)	[77]

Microwave heating has also been found to be advantageous for the synthesis of supramolecular compounds. Ott *et al.* reported a method for preparing PS$_n$-[Ru]-PEG$_{70}$ block copolymer (PS: polystyrene and PEG: polyethylene glycol), as shown in Scheme **4** [26]. They optimized the reaction conditions by varying the reaction time, solvent, and temperature. First, they set the reaction time to 1 h because longer reaction times did not lead to an increase in the conversion yield from the starting *mono*-complex **8** to the desired *bis*-complex **9**; however, this resulted in the decomposition of **8**, as determined by gel permeation chromatography (GPC) analyses. In addition, **9** was obtained in a higher yield when the reaction temperature was increased from 80°C to 110°C; however, higher temperatures also led to the decomposition of **8**. Moreover, changing the reaction solvent from chloroform to THF/MeOH mixture provided a better conversion yield of up to 73%. Because the concentration of the substrate in the reaction mixture is also an important factor increasing the yield of **9**; thus, a higher content of methanol, which is a major precipitant of polymers, is not preferable. However, methanol plays the important role of a reducing agent in the reduction of ruthenium ions from Ru(III) to Ru(II) in the reaction. Finally, the reaction conditions were optimized as shown in Scheme **4**. These optimization processes were carried out for the microwave irradiation technique by accurately controlling the reaction time and temperature using a microwave synthesizer. Microwave heating appears to be a much better alternative for reactions that involve undesirable decomposition, as mentioned above, because conventional heating methods may require longer reaction times and result in low yields.



8 **9**

Scheme 4.

Table 4. List of Microwave-Assisted Syntheses of Group 9 Metal Complexes

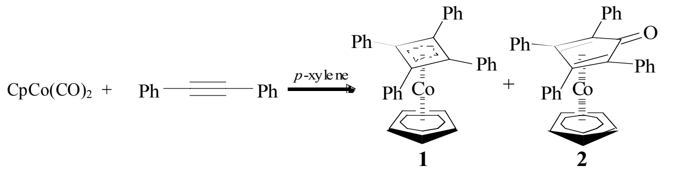
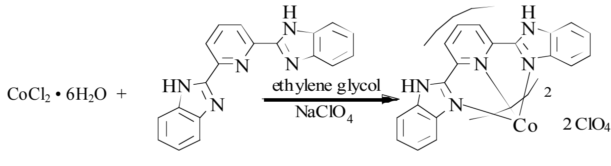
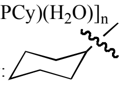
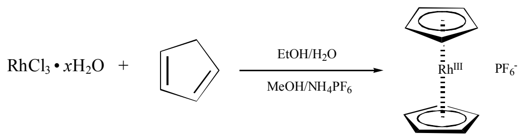
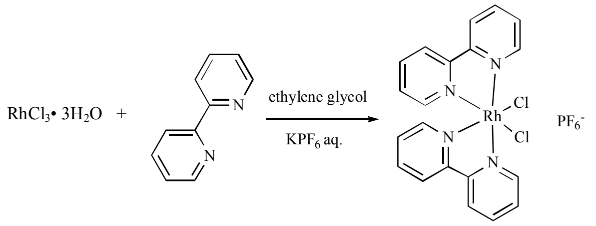
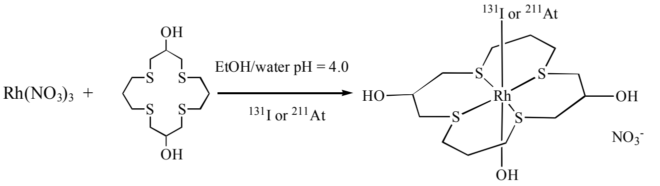
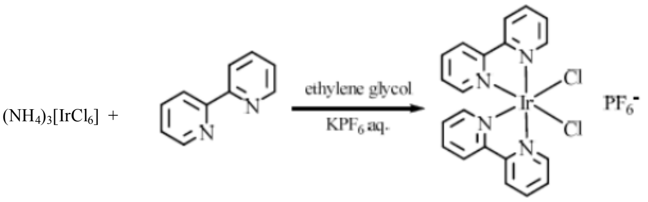
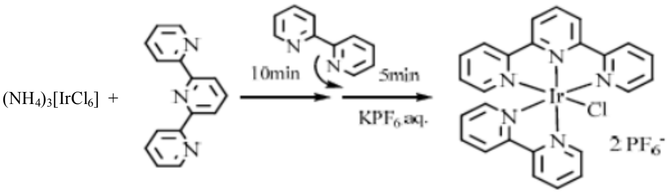
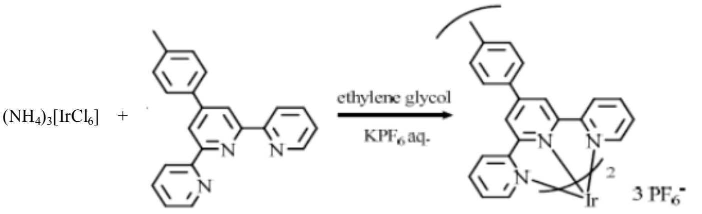
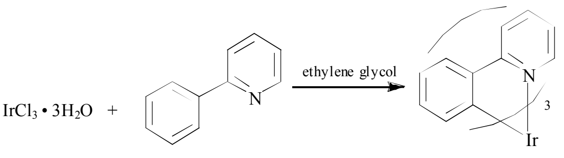
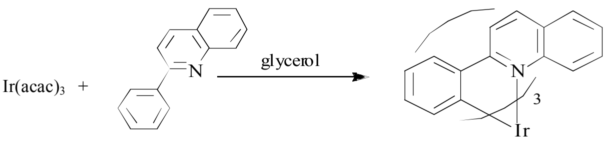
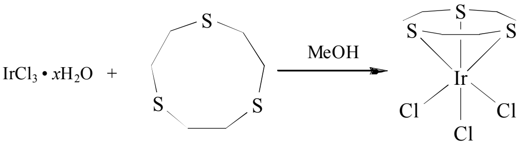
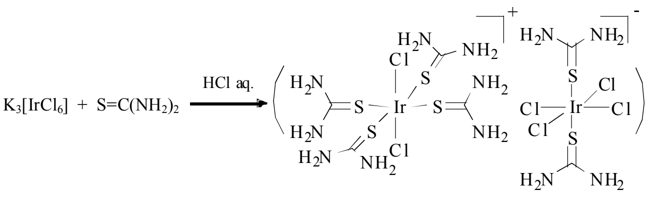
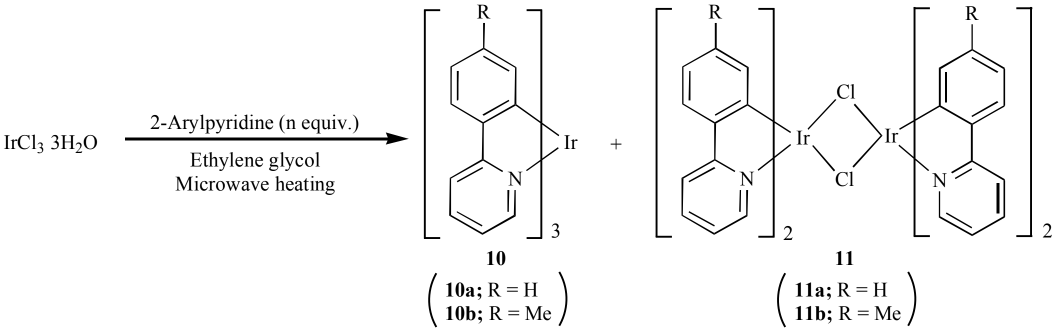
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Co	η-arene complex	10 min, yields = 3–52% for 1 and 14–85% for 2 (7 examples)	[78]
	Co	N-coordinated complex	25 min, yield = 57% (1 example)	[79]
$CoSO_4 \cdot 7H_2O + CyP(O)(OH)_2 \xrightarrow{water} [Co(O_3PCy)(H_2O)]_n$ Cy: 	Co	P-coordinated complex	10 min, yield not given (1 example)	[80]
	Rh	η-arene complex	30 s, yield = 62% (1 example)	[12]
	Rh	N-coordinated complex	75 s–4 min, yields = 65–86% (3 examples)	[81]

Table 4. contd….

Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Rh	S-coordinated complex	35 min, yields = 83–90% (2 examples)	[82]
	Ir	N-coordinated complex	15 min, yields = 43–65% (6 examples)	[83]
	Ir	N-coordinated complex	15 min (total), yields = 30–65% (7 examples)	[84]
	Ir	N-coordinated complex	15 min, yields = 18–63% (4 examples)	[85]
	Ir	cyclometallated complex	1 min, yields = 75% (2 examples)	[86]
	Ir	cyclometallated complex	30 min, yields = 10–40% (4 examples)	[87]
	Ir	S-coordinated complex	70 min, yields = 96% (1 example) in Ref. [19]; 16–150 s, 49–98% (2 examples) in Ref. [88]	[19], [88]
	Ir	S-coordinated complex	1 min, yield not given (1 example)	[89]



Entry	R	n^a	Reaction time (min)	Ratios^b
				10:11
1	H	100	1	100:0
2	H	50	3	100:0
3	H	30	30	55:45
4	H	10	30	0:100
5	Me	100	3	100:0
6	Me	10	30	0:100

[a] Molar ratio of the ligand *vs.* $IrCl_3$ $3H_2O$ used.

[b] Ratios determined from the integrals of the ^1H NMR spectra.

Scheme 5.

Group 9 Metal Complexes

Selected reaction schemes involving the microwave-assisted synthesis of group 9 metal complexes are summarized in Table **4**. Cyclometallated iridium complexes such as *fac*-[Ir(ppy)$_3$] (**10a**; ppyH = 2-phenylpyridine) have attracted considerable attention as phosphors for use in organic light-emitting diodes (OLEDs). Numerous cyclometallated iridium(III) complexes with various organic ligands have already been reported in the last decade. Although iridium chloride reacts with 2-arylpyridine under reflux conditions, the undesired dichlorobridged dimer **11** is the main product, with only a small amount of the tris- cyclometallated complex (10%) being produced. In general, the syntheses of iridium complexes require long reaction times at high temperatures and result in low yields. We have studied the reaction of iridium chloride with 2-arylpyridine and reported the selective one-pot synthesis of tris-cyclometallated iridium complexes using microwave irradiation [86]. This new synthetic route does not require column chromatography for purification. It should be noted that the product distribution between the formation of **10** and **11** was strongly dependent on the amount of 2-arylpyridine in the solution, as shown in Scheme **5**. When a large excess of 2-arylpyridine (100 times molar excess) was used, **10a** was produced with a yield of 75% after microwave irradiation for 1 min. When a 10-fold excess amount of 2-phenylpyridine was used, however, 100% of **11a** remained even after microwave irradiation for 30 min, indicating that 2-phenylpyridine acted not only as a ligand but also as a base that traps protons in the solution. Since the deprotonation of 2-phenylpyridine is essential for its coordination to the iridium(III) center, a base should be required for the one-pot synthesis of **10a**. This synthetic method can probably be applied to other cyclometallated iridium complexes for use in OLEDs.

Group 10 Metal Complexes

Selected reaction schemes involving the microwave-assisted synthesis of group 10 metal complexes are summarized in Table **5**. Castan *et al.* reported the novel cyclometallation of palladium and platinum complexes in the solid state, as shown in Scheme **6** [91]. The complexes [M(2,4′-bpyMe)X$_3$] (M = Pd, Pt; X = Cl, Br) released one molecule of HX under microwave irradiation to give cyclometallated complexes [M(2,4′-bpyMe-H)X$_2$]. The reactions were investigated by thermal analysis (TGA, DTA, and DSC). The results indicate that one molecule of HX was released from [M(2,4′-bpyMe)X$_3$] in the temperature range of 160–260 °C with concomitant cyclometallation to give [M(2,4′-bpyMe-H)X$_2$]. The ease of cyclometallation was found to be in the order Pd > Pt and Cl > Br. Upon irradiation in a microwave oven, [M(2,4′-bpyMe)X$_3$] can also be transformed to [M(2,4′-bpyMe-H)X$_2$]. Interestingly, the rate of reaction depends on the irradiation mode used. A multi-mode reactor did not work in the case of solid-state irradiation since the particle was not large enough to absorb the microwave. The use of vermiculite as a supporter to absorb microwaves afforded good heating; however, the reaction time was consistent with that of conventional heating, which was as long as 1 h. On the other hand, a single-mode apparatus could heat the [M(2,4′-bpyMe)X$_3$] complex in the solid state without any supporter, resulting in reaction times as short as 1–5 minutes. By using this technique, a rapid and quantitative cyclometallation of the complexes could be achieved, and this result is now attributed exclusively to a microwave effect.

4. SUMMARY

In recent times, metal complexes have been attracting increasing attention because of the characteristics they exhibit as functional materials. One of the most basic approaches employed to study metal complexes is design and synthesis, and by using this approach, various compounds have been synthesized. For the past several decades, microwave heating has been one of the most widely studied techniques as a tool for facilitating reactions in synthetic chemistry. In this review, we described the microwave-assisted synthesis of metal complexes. More than 20 years have passed since the first metal complexes were synthesized by microwave heating. During this period, majority of the microwave reactors were obtained by modifying domestic microwave ovens. Microwave heating contributes to the synthesis of metal complexes not only by reducing the reaction time but also by increasing the yield and selectivity through suppression of undesirable side reactions. This technique will aid researchers in synthesizing materials whose

Table 5. List of Microwave-Assisted Syntheses of Group 10 Metal Complexes

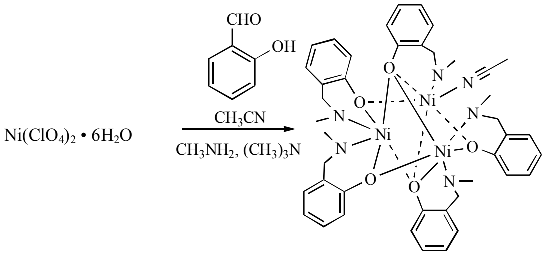
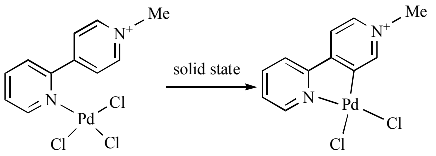
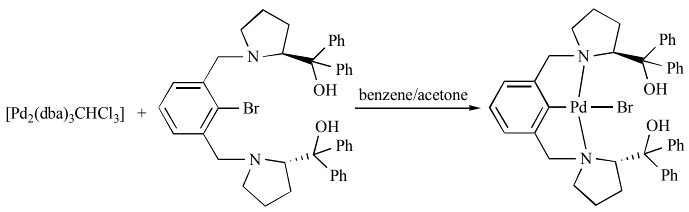
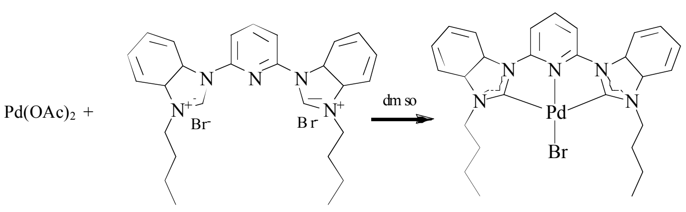
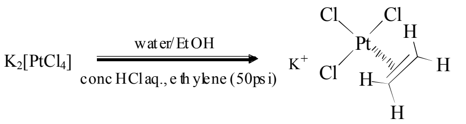
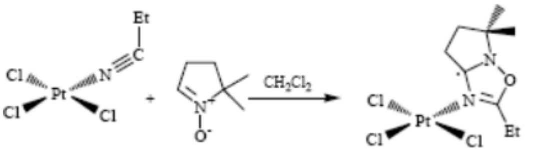
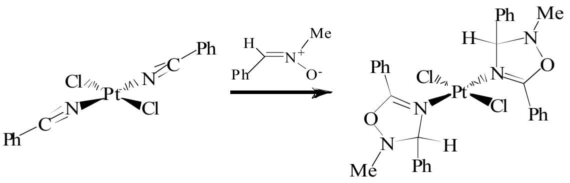
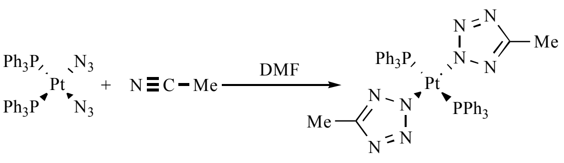
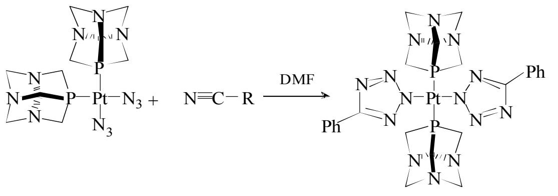
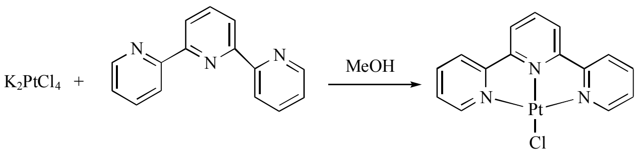
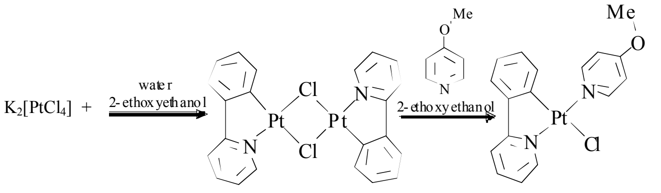
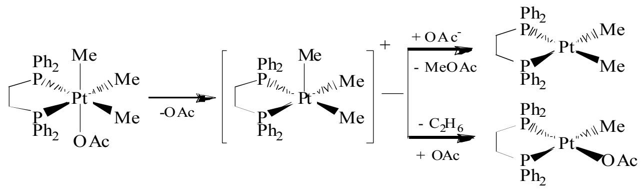
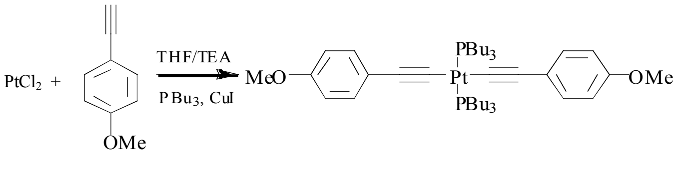
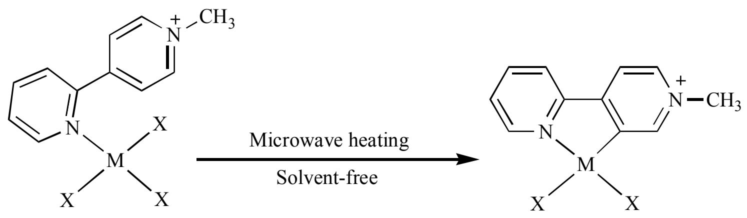
Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Ni	cluster complex	29 min, yield = 87% (1 example)	[90]
	Pd	cyclometallated complex	1–5 min, yields not given (3 examples)	[91]
	Pd	cyclometallated complex	10 min, yield = 79% (1 example)	[92]
	Pd	carbene complex	25 min, yield = 75% (1 example)	[93]
	Pt	η-arene complex	15 min, yield = 89% (1 example)	[94]
	Pt	N-coordinated complex	10 min–3 h, yields = 62–90% (4 examples)	[95]
	Pt	N-coordinated complex	170 min (total), yields = 68–76% (5 examples) in Ref. [96]; 1 h, 55–60% (4 examples) in Ref. [97]; 1–2 min, 75% (12 examples) in Ref. [98]	[96], [97], [98]
	Pt	N-coordinated complex	1 h, yields = 35-65% (8 examples) in Ref. [99]; 1 h, yield not given (1 example) in Ref. [100]	[99], [100]

Table 5. contd….

Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Pt	N-coordinated complex	1 h, yields = 58–65% (3 examples)	[101]
	Pt	N-coordinated complex	1 min, yields = 37–47% (2 examples)	[88]
	Pt	cyclometallated complex	1–6 min, yields = 55–94% (5 examples)	[102]
	Pt	P-coordinated complex	4–40 h, rate constants (k_{obs}) and the product selectivities of the reactions are discribed	[103]
	Pt	P-coordinated complex	6 min–1 h, yields = 47–76% (8 examples)	[104]

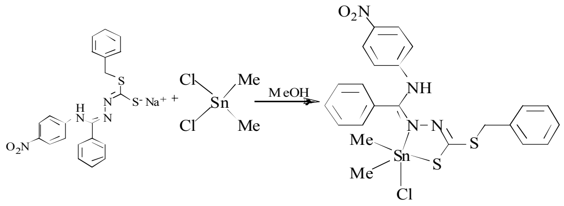
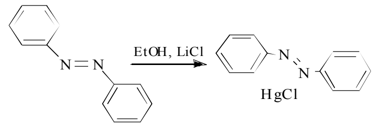
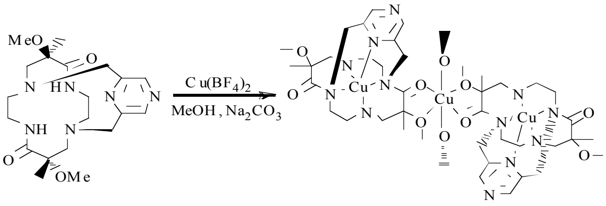
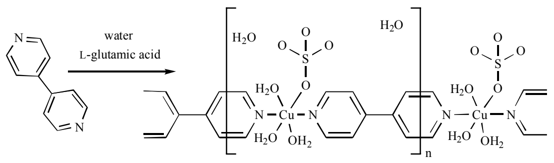
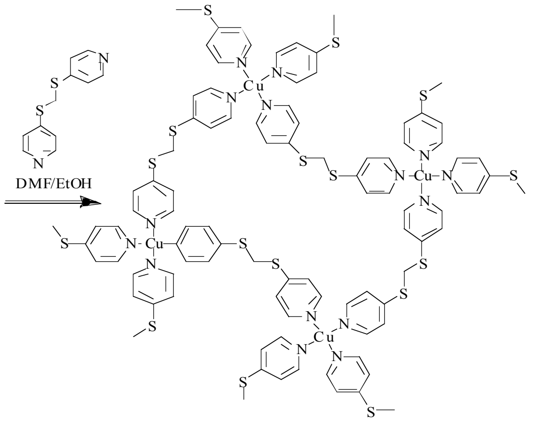
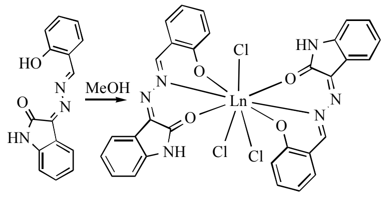
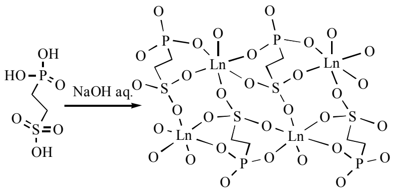


Entry	M	X	Irradiation time[a] (min)	
			multi-mode	single-mode
1	Pd	Cl	15	1
2	Pt	Cl	60	5
3	Pd	Br	60	5

[a] The irradiation times for complete reaction.

Scheme 6.

Table 6. List of Microwave-Assisted Syntheses of other Groups Metal Complexes

Reaction Scheme	Metal	Type of Product	Reaction Time and Yields (Number of Examples)	Ref.
	Sn	N-coordinated complex	8 min, yields not given (8 examples)	[105]
$Hg(OAc)_2$ + 	Hg	mercurated complex	30–47 min, yields = 29–33% (2 examples)	[13]
	Cu	cluster complex	1 min, yield = 86% (1 example)	[106]
$CuSO_4 \cdot 5H_2O$ + 	Cu	cluster complex	3 min, yield not given (1 example)	[107]
$Cu(NO_3)_2 \cdot 3H_2O$ 	Cu	cluster complex	1.5 min, yield = 69% (1 example)	[108]
$LnCl_3 \cdot xH_2O$ +  Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) or Gd(III)	Ln	N-coordinated complex	2 min, yields = 63–70% (7 examples)	[109]
LnX_3 +  Ln = Ho(III), Er(III), Tm(III), Yb(III), Lu(III) or Y(III) X = NO_3, Cl or CH_3COO	Ln	cluster complex	2 h, yields = 25–56% (6 examples)	[110]

synthesis might otherwise be difficult by conventional thermal heating methods.

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REFERENCES

[1] Streitwieser, A.; Ward, H. R. Organic compounds in microwave discharge. *J. Am. Chem. Soc.*, **1962**, *84*, 1065-1066.

[2] Liu, S. W.; Wightman, J. P. Decomposition of simple alcohols, ethers and ketones in a microwave discharge. *J. Appl. Chem. Biotechnol.*, **1971**, *21*, 168-172.

[3] Hesek, J. A.; Wilson, R. C. Use of microwave oven in in-process control. *Anal. Chem.*, **1974**, *46*, 1160.

[4] Abu-Samra, A.; Morris, J. S.; Koirtyohann, S. R. Wet ashing of some biological samples in a microwave oven. *Anal. Chem.*, **1975**, *47*, 1475-1477.

[5] Barrett, P.; Davidowski, L. J.; Penaro, K. W.; Copeland, T. R. Microwave oven-based wet digestion technique. *Anal. Chem.*, **1978**, *50*, 1021-1023.

[6] Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J. The use of microwave ovens for rapid organic synthesis. *Tetrahedron Lett.*, **1986**, *27*, 279-282.

[7] Giguere, R. J.; Bray, T. L.; Duncan, S. M.; Majetich, G. Application of commercial microwave ovens to organic synthesis. *Tetrahedron Lett.*, **1986**, *27*, 4945-4948.

[8] Mingos, D. M. P.; Baghurst, D. R. Applications of microwave dielectric heating effects to synthetic problems in chemistry. *Chem. Soc. Rev.*, **1991**, *20*, 1-47.

[9] Galema, S. A. Microwave chemistry. *Chem. Soc. Rev.*, **1997**, *26*, 233-238.

[10] Gabriel, C.; Gabriel, S.; Grant, E. H.; Halstead, B. S. J.; Mingos, D. M. P. Dielectric parameters relevant to microwave dielectric heating. *Chem. Soc. Rev.*, **1998**, *27*, 213-223.

[11] de la Hoz, A.; Díaz-Ortiz, Á.; Moreno, A. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chem. Soc. Rev.*, **2005**, *34*, 164-178.

[12] Baghurst, D. R.; Mingos, D. M. P.; Watson, M. J. Application of microwave dielectric loss heating effects for the rapid and convenient synthesis of oraganometallic compounds. *J. Organomet. Chem.*, **1989**, *368*, C43-C45.

[13] Ali, M.; Bond, S. P.; Mbogo, S. A.; McWhinnie, W. R.; Watts, P. M. Use of a domestic microwave oven in organometallic chemistry. *J. Organomet. Chem.*, **1989**, *371*, 11-13.

[14] O'Regan, B.; Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature*, **1991**, *353*, 737-740.

[15] (a) Fujita, E. Photochemical carbon dioxide reduction with metal complexes. *Coord. Chem. Rev.*, **1999**, *185*, 373-384. (b) Abe, T.; Shinozaki, K. Tuning of luminescent spectra of neutral ruthenium(II) complexes by crystal waters. *Inorg. Chem.*, **2005**, *44*, 849-851. (c) Abe, T.; Itakura, T.; Ikeda, N.; Shinozaki, K. Luminescence color change of a platinum(II) complex solid upon mechanical grinding. *Dalton Trans.*, **2009**, 711-715. (d) Abe, T.; Suzuki,T.; Shinozaki, K. Luminescence change by the solvent of crystallization, solvent reorganization and vapochromism of neutral dicyanoruthenium(II) complex in the solid state. *Inorg. Chem.*, **2010**, *49*, 1794-1800. (e) Matsubara, Y.; Konno, H.; Kobayashi, A.; Ishitani, O. Quantitative Photochemical Formation of $[Ru(tpy)(bpy)H]^+$. *Inorg. Chem.*, **2009**, *48*, 10138-10145. (f) Kobayashi, A.; Konno, H.; Sakamoto, K.; Sekine, A.; Ohashi, Y.; Iida, M.; Ishitani, O. Transition metal complexes coordinated by an NAD(P)H model compound and their enhanced hydride-donating abilities in the presence of a base. *Chem. Eur. J.*, **2005**, *11*, 4219-4226. (g) Konno, H.; Kobayashi, A.; Sakamoto, K.; Fagalde, F.; Katz, N. E.; Saitoh, H.; Ishitani, O. Synthesis and properties of $[Ru(tpy)(4,4'\text{-}X_2bpy)H]^+$ (tpy = 2,2':6',2''-terpyridine, bpy-2,2'-bipyridine, X = H and MeO), and their reactions with CO_2. *Inorg. Chim. Acta*, **2000**, *299*, 155–163. (h) Konno, H.; Sakamoto, K.; Ishitani, O. Regiospecific hydride transfer from *cis*-$[Ru(bpy)_2(CO)(CHO)]^+$ to NAD^+ model compounds: a model for enzymatic reactions by aldehyde dehydrogenases. *Angew. Chem., Int. Ed.*, **2000**, *39*, 4061–4063. (i) Kobayashi, A.; Takatori, R.; Kikuchi, I.; Konno, H.; Sakamoto, K.; Ishitani, O. Formation of novel 1:1 adducts accompanied by regioselective hydride transfer from transition-metal hydrido complexes to NAD(P) models. *Organometallics*, **2001**, *20*, 3361–3363. (j) Konno, H.; Ishii, Y.; Sakamoto, K.; Ishitani, O. Synthesis, spectroscopic characterization, electrochemical and photochemical properties of ruthenium(II) polypyridyl complexes with a tertiary amine ligand. *Polyhedron*, **2002**, *21*, 61-68.

[16] Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. Homogeneous asymmetric hydrogenation of functionalized ketones. *J. Am. Chem. Soc.*, **1988**, *110*, 629-631.

[17] Miyaura, N.; Suzuki, A. Palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chem. Rev.*, **1995**, *95*, 2457-2483.

[18] Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E. Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature*, **1998**, *395*, 151-154.

[19] Baghurst D. R.; Mingos, D. M. P. A new reaction vessel for accelerated syntheses using microwave dielectric super-heating effects. *J. Chem. Soc. Dalton Trans.*, **1992**, *7*, 1151-1155.

[20] Baghurst. D. R.; Mingos, D. M. P. Design and application of a reflux modification for the synthesis of organometallic compounds using microwave dielectric loss heating effects. *J. Organomet. Chem.*, **1990**, *384*, C57-C60.

[21] Matsumura-Inoue, T.; Tanabe, M.; Minami, T.; Ohashi, T. A remarkably rapid synthesis of ruthenium(II) polypyridine complexes by microwave irradiation. *Chem. Lett.*, **1994**, *23*, 2443-2446.

[22] Whittaker, A. G.; Mingos, D. M. P. Synthetic reactions using metal powders under microwave irradiation. *J. Chem. Soc. Dalton Trans.*, **2002**, 3967-3970.

[23] Ardon, M.; Hayes, P. D.; Hogarth, G. Microwave-assisted reflux in organometallic chemistry: synthesis and structural determination of molybdenum carbonyl complexes. *J. Chem. Educ.*, **2002**, *79*, 1249-1251.

[24] Broomhead, J. A.; Young, C. G. Tris(2,2'-bipyridine)ruthenium(II) dichloride hexahydrate. *Inorg. Synth.*, **1982**, *21*, 127-128.

[25] Johnson, S. R.; Westmoreland, T. D.; Caspar, J. V.; Barqawi, K. R.; Meyer, T. J. Influence of variations in the chromophoric ligand on the properties of metal-to-ligand charge-transfer excited states. *Inorg. Chem.*, **1988**, *27*, 3195-3200.

[26] Ott, C.; Wouters, D.; Thijs, H. M. L.; Schubert, U. S. New preparation and purification methods for metallo-supramolecular block copolymers. *J. Inorg. Organomet. Polym.*, **2007**, *17*, 241-249.

[27] Ardon, M.; Hogarth, G.; Oscroft, D. T. W. Organometallic chemistry in a conventional microwave oven: the facile synthesis of group 6 carbonyl complexes. *J. Organomet. Chem.*, **2004**, *689*, 2429-2435.

[28] Barnard, T. M. and Leadbeater, N. E. Real-time monitoring of microwave-promoted organometallic ligand substitution reactions using in *situ* Raman spectroscopy. *Chem. Commun.*, **2006**, *34*, 3615-3616.

[29] Coelho, A. C.; Almeida Paz, F. A.; Klinowski, J.; Pillinger, M.; Gonçalves, I. S. Microwave assisted synthesis of molybdenum and tungsten tetracarbonyl complexes with a pyrazoylpyridine ligand. Crystal structure of *cis*-$[Mo(CO)_4\{ethyl[3\text{-}(2\text{-}pyridyl)\text{-}1\text{-}pyrazoyl]acetate\}]$. *Molecules*, **2006**, *11*, 940-952.

[30] Amarante, T. R.; Paz, F. A. A.; Gago, S.; Gonçalves, I. S.; Pillinger, M.; Rodrigues, A. E.; Abrantes, M. Microwave-assisted synthesis and crystal structure of oxo(diperoxo)(4,4'-di-*tert*-butyl-2,2'-bipyridine)-molybdenum(VI). *Molecules*, **2009**, *14*, 3610-3620.

[31] Adil, K.; Marrot, J.; Leblanc, M.; Maisonneuve, V. Bis[tris(2-aminoethyl)amine] bis(pentafluoridooxidomolybdate) difluoride monohydrate. *Acta Cystallogr., Sect. E: Struct. Rep. Online*, **2007**, *E63*, m1511-m1513.

[32] Artillo, A.; Sala, G. D.; De Santis, M.; Llordes, A.; Ricart, S.; Spinella, A. Preparation of organometallic uracil-analogue Fischer carbene complexes: comparative study of conventional heating vs microwave heating. *J. Organomet. Chem.*, **2007**, *692*, 1277-1284.

[33] Dabirmanesh, Q.; Roberts, R. M. G. The application of microwave dielectric heating to the synthesis of arene-metal complexes. Synthesis of $[(\eta\text{-arene})(CO)_3Mn]PF_6$ complexes and $[(\eta\text{-arene})(\eta\text{-cyclopentadienyl})Fe][PF_6]$ complexes with triphenylphosphine, *tert*-butylbenzenes and a sterically hindered phenol as arene ligands. *J. Organomet. Chem.*, **1997**, *542*, 99-103.

[34] Milios, C. J.; Vinslava, A.; Whittaker, A. G.; Parsons, S.; Wernsdorfer, W.; Christou, G.; Perlepes, S. P.; Brechin, E. K. Microwave-assisted synthesis of a hexanuclear Mn^{III} single-molecule magnet. *Inorg. Chem.*, **2006**, *45*, 5272-5274.

[35] Bhojak, N.; Gudasaria, D. D.; Khiwani, N.; Jain, R. Microwave assisted synthesis spectral and antibacterial investigations on complexes of Mn(II) with amide containing ligands. *E-J. Chem.*, **2007**, *4*, 232-237.

[36] Causey, P. W.; Besanger, T. R.; Schaffer, P.; Valliant, J. F. Expedient multi-step synthesis of organometallic complexes of Tc and Re in high effective specific activity. A new platform for the production of molecular imaging and therapy agents. *Inorg. Chem.*, **2008**, *47*, 8213-8221.

[37] Nagao, H.; Nishimura, H.; Kitanaka, Y.; Howell, F. S.; Mukaida, M.; Kakihana, H. Selective formation of ruthenium(IV) complexes with a monooxygen ligand: *trans*-$[RuX(O)(py)_4]^+$ (X = C1, ONO). *Inorg. Chem.*, **1990**, *29*, 1693-1700.

[38] Togano, T.; Nagao, N.; Tsuchida, M.; Kumakura, H.; Hisamatsu, K.; Howell, F. S.; Mukaida, M. One-pot and selective synthesis of a series of $[RuCl_{6\text{-}2n}L_n]$ (L= bidentate ligand, n = 0-3) types of complexes with polypyridyl ligands; another example of the synthetic utility of 'ruthenium-blue' solution. *Inorg. Chim. Acta*, **1992**, *195*, 221-225.

[39] A mixture of $RuCl_3{\cdot}nH_2O$ (200 mg, 0.76 mmol) and Hdpa (395 mg, 2.31 mmol) in ethylene glycol (20 ml) was set in a 50 ml round flask and placed in inert atmosphere by bubbling dry nitrogen gas. The mixture was refluxed using either microwave irradiation employing EYELA MWO-1000S (200 W) or a preheated oil bath (~200 °C) for 20 min; then, the mixture was immediately cooled on an ice bath to quench the reaction after heating. The solution was poured into 100 ml of 0.1 M KPF_6 solution. The precipitated PF_6^- salt of **1** was collected by filtration and washed with hot water and ether. The crude product was dried and then purified by recrystallization using CH_3CN-ether and/or by column chromatography on neutral aluminum oxide (eluent

CH_3CN). The isolated yields are 86% and 42%, respectively. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.98 (brs, NH), 8.13 (d, 6H, py), 7.94 (t, 6H, py), 7.20 (d, 6H, py), 6.91 (t, 6H, py). MS (ESI): *m/z* = 172 $[L + H]^+$; 307 $[M]^{2+}$; 443 $[M – L]^+$

[40] Kunz, P. C.; Berghahn, M.; Brückmann, N. E.; Dickmeis, M.; Kettel, M.; Spingler, B. Functionalised tris(pyrazolyl)methane ligands and $Re(CO)_3$ complexes thereof. *Z. Anorg. Allg. Chem.*, **2009**, *635*, 471-478.

[41] Green, A. E. C.; Causey, P. W.; Louie, A. S.; Armstrong, A. F.; Harrington, L. E. and Valliant, J. F. Microwave-assisted synthesis of 3,1,2- and 2,1,8-Re(I) and ^{99m}Tc(I)-metallocarborane complexes. *Inorg. Chem.*, **2006**, *45*, 5727-5729.

[42] Armstrong, A. F.; Valliant, J. F. Microwave-assisted synthesis of tricarbonyl rhenacarboranes: steric and electronic effects on the 1,2 → 1,7 carborane cage isomerization. *Inorg. Chem.*, **2007**, *46*, 2148-2158.

[43] Dabirmanesh, Q.; Roberts, R. M. G. The synthesis of iron sandwich complexes by microwave dielectric heating using a simple solid CO_2-cooled apparatus in an unmodified commercial microwave oven. *J. Organomet. Chem.*, **1993**, *460*, C28-C29.

[44] Dabirmanesh, Q.; Fernando, S. I. S.; Roberts, R. M. G. Synthesis and decomplexation of (η-arene)(η-cyclopentadienyl)iron(II) hexafluorophosphates using microwave dielectric heating. *J. Chem. Soc. Perkin Trans. 1*, **1995**, 743-749.

[45] Roberts, R. M. G. Synthesis of (η^6-arene)(η^5-cyclopentadienyl) iron(II) complexes with heteroatom and carbonyl substituents. Part I: oxygen and carbonyl substituents. *J. Organomet. Chem.*, **2006**, *691*, 2641-2647.

[46] Garringer, S. M.; Hesse, A. J.; Magers, J. R.; Pugh, K. R.; O'Reilly, S. A.; Wilson, A. M. Microwave synthesis of benchmark organo-iron complexes. *Organometallics*, **2009**, *28*, 6841-6844.

[47] Puciová, M.; Ertl, P.; Toma, Š. Synthesis of ferrocenyl- substituted heterocycles: the beneficial effect of the microwave irradiation. *Collect. Czech. Chem. Commun.*, **1994**, *59*, 175-185.

[48] Villemin, D.; Martin, B.; Puciova, M.; Toma, S. Dry synthesis under microwave irradiation: synthesis of ferrocenylenons. *J. Organomet. Chem.*, **1994**, *484*, 27-31.

[49] Janková, Š.; Císařová, I.; Uhlík, F.; Štepnička, P.; Kotora, M. Synthesis and characterisation of Dewar benzene-ferrocene conjugates. *Dalton Trans.*, **2009**, *17*, 3137-3139.

[50] Barghurst, D. R.; Mingos, D. M. P. Design and application of a reflux modification for the synthesis of organometallic compounds using microwave dielectric loss heating effects. *J. Organomet. Chem.*, **1990**, *384*, C57-C60.

[51] Kuhnert, N.; Danks, T. N. Microwave accelerated synthesis of cyclopentadienyl bis-phosphine ruthenium(II) thiolato complexes using focused microwave irradiation. *J. Chem. Res. (S)*, **2002**, 66-68.

[52] Albrecht, C.; Gauthier, S.; Wolf, J.; Scopelliti, R.; Severin, K. Microwave-assisted organometallic syntheses: formation of dinuclear $[(arene)Ru(\mu\text{-}Cl)_3RuCl(L\text{-}L')]$ complexes (L-L': chelate ligands with *P*-, *N*-, or *S*-donor atoms) by displacement of arene π ligands. *Eur. J. Inorg. Chem.*, **2009**, *8*, 1003-1010.

[53] Bolink, H. J.; Cappelli, L.; Coronado, E.; Grätzel, M.; Nazeeruddin, Md. K. Efficient and stable solid-state light-emitting electrochemical cell using tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) hexafluorophosphate. *J. Am. Chem. Soc.*, **2006**, *128*, 46-47.

[54] Greene, D. L.; Mingos, D. M. P. Application of microwave dielectric loss heating effects for the rapid and convenient synthesis of ruthenium(II) polypyridine complexes. *Trans. Met. Chem.*, **1991**, *16*, 71-72.

[55] Beves, J. E.; Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schaffner, S.; Zampese, J. A. 4'-chloro-2,2':6',2''-terpyridine (L): ethyl sulfate salts of $[H_2L]^{2+}$ and the single crystal structures of $[H_2L][EtOSO_3]Cl\cdot H_2O$ and $[ML_2][PF_6]$ with M = Fe and Ru. *Inorg. Chem. Commun.*, **2008**, *11*, 1006-1008.

[56] Martineau, D.; Beley, M.; Gros, P. C.; Cazzanti, S.; Caramori, S.; Bignozzi, C. A. Tuning of ruthenium complex properties using pyrrole- and pyrrolidine-containing polypyridine ligands. *Inorg. Chem.*, **2007**, *46*, 2272-2277.

[57] Jasimuddin, Sk.; Byabartta, P.; Mostafa, G.; Lu, T.-H.; Sinha, C. Synthesis, spectral studies, crystal structure and redox properties of homoleptic tris-chelated ruthenium(II)-arylazoimidazol. *Polyhedron*, **2004**, *23*, 727-733.

[58] Grabulosa, A.; Beley, M.; Gros, P. C. Remarkable effect of 4-substituted 2,2'-bipyridine ligands on the stereochemistry of ruthenium(II) complexes. *Eur. J. Inorg. Chem.*, **2008**, *11*, 1747-1751.

[59] Wu, F.; Thummel, R. P. Ru(II) complexes of crowded delocalized diimine ligands. *Inorg. Chim. Acta*, **2002**, *327*, 26-30.

[60] Glasson, C. R. K.; Meehan, G. V.; Clegg, J. K.; Lindoy, L. F.; Smith, J. A.; Keene, F. R.; Motti, C. Microwave synthesis of a rare $[Ru_2L_3]^{4+}$ triple helicate and its interaction with DNA. *Chem. Eur. J.*, **2008**, *14*, 10535-10538.

[61] Xiao, X.; Sakamoto, J.; Tanabe, M.; Yamazaki, S.; Yamabe, S.; Matsumura-Inoue, T. Microwave synthesis and electrospectrochemical study on ruthenium(II) polypyridine complexes. *J. Electroanal. Chem.*, **2002**, *527*, 33-40.

[62] Rau, S.; Schäfer, B.; Grüssing, A.; Schebesta, S.; Lamm, K.; Vieth, J.; Görls, H.; Walther, D.; Rudolph, M.; Grummt, U. W.; Birkner, E. Efficient synthesis of ruthenium complexes of the type $(R\text{-}bpy)_2RuCl_2$ and $[(R\text{-}bpy)_2Ru(L\text{-}L)]Cl_2$ by microwave-activated reactions (R: H, Me, *tert*-But) (L-L: substituted bibenzimidazoles, bipyrimidine, and phenanthroline). *Inorg. Chim. Acta*, **2004**, *357*, 4496-4503.

[63] Schwalbe, M.; Schäfer, B.; Görls, H.; Rau, S.; Tschierlei, S.; Schmitt, M.; Popp, J.; Vaughan, G.; Henry, W.; Vos, J. G. Synthesis and characterisation of poly(bipyridine)ruthenium complexes as building blocks for heterosupramolecular arrays. *Eur. J. Inorg. Chem.*, **2008**, *21*, 3310-3319.

[64] Abrahamsson, M.; Jäger, M.; Österman, T.; Eriksson, L.; Persson, P.; Becker, H. C.; Johansson, O.; Hammarström, L. A 3.0μs room temperature excited state lifetime of a bistridentate RuII-polypyridine complex for rod-like molecular arrays. *J. Am. Chem. Soc.*, **2006**, *128*, 12616-12617.

[65] Abrahamsson, M.; Jäger, M.; Kumar, R. J.; Österman, T.; Persson, P.; Becker, H. C.; Johansson, O.; Hammarström, L. Bistridentate ruthenium(II)polypyridyl-type complexes with microsecond ^{3}MLCT state lifetimes: sensitizers for rod-like molecular arrays. *J. Am. Chem. Soc.*, **2008**, *130*, 15533-15542.

[66] Jäger, M.; Kumar, R. J.; Görls, H.; Bergquist, J.; Johansson, O. Facile synthesis of Bistridentate Ru^{II} complexes based on 2,6-di(quinolin-8-yl)pyridyl ligands: sensitizers with microsecond ^{3}MLCT excited state lifetimes. *Inorg. Chem.*, **2009**, *48*, 3228-3238.

[67] Sasaki, I.; Daran, J. C.; Aït-Haddou, H.; Balavoine, G. G. A. New annelated 2,2':6',2''-terpyridines and their Ru(II) complexes: synthesis and characterization. *Inorg. Chem. Commun.*, **1998**, *1*, 354-357.

[68] Ziegler, M.; Monney, V.; Stoeckli-Evans, H.; Von Zelewsky, A.; Sasaki, I.; Dupic, G.; Daran, J. C.; Balavoine, G. G. A. Complexes of new chiral terpyridyl ligands. Synthesis and characterization of their ruthenium(II) and rhodium(III) complexes. *J. Chem. Soc. Dalton Trans.*, **1999**, 667-675.

[69] Funaki, T.; Yanagida, M.; Onozawa-Komatsuzaki, N.; Kasuga, K.; Kawanishi,Y.; Kurashige, M.; Sayama, K.; Sugihara, H. Synthesis of a new class of cyclometallated ruthenium(II) complexes and their application in dye-sensitized solar cells. *Inorg. Chem. Commun.*, **2009**, *12*, 842-845.

[70] Pezet, F.; Daran, J. C.; Sasaki, I.; Aït-Haddou, H.; Balavoine, G. G. A. Highly diastereoselective preparation of ruthenium bis(diimine) sulfoxide complexes: new concept in the preparation of optically active octahedral ruthenium complexes. *Organometallics*, **2000**, *19*, 4008-4015.

[71] Munery, S.; Jaud, J.; Bonvoisin, J. Synthesis and characterization of bis(bipyridine)ruthenium(II) complexes with bromo or protected ethynyl β-diketonato ligands. *Inorg. Chem. Commun.*, **2008**, *11*, 975-977.

[72] Díaz-Valenzuela, M. B.; Phillips, S. D.; France, M. B.; Gunn, M. E.; Clarke, M. L. Enantioselective hydrogenation and transfer hydrogenation of bulky ketones catalyzed by a ruthenium complex of a chiral tridentate ligand. *Chem. Eur. J.*, **2009**, *15*, 1227-1232.

[73] Bashilov, A. V.; Fedorova, A. A.; Runov, V. K. Reduction of ruthenium(IV) to ruthenium(III) in aqueous alcohol solutions of hydrochloric acid under microwave radiation. *J. Anal. Chem.*, **2000**, *55*, 1123-1155.

[74] Ezerskaya, N. A.; Toropchenova, E. S.; Pachgin, D. B.; Kiseleva, I. N. Controlled-potential coulometric determination of ruthenium in $Ru(OH)Cl_3$ with microwave sample preparation. *J. Anal. Chem.*, **2004**, *59*, 296-298.

[75] Leadbeater, N. E.; Shoemaker, K. M. Preparation of ruthenium and osmium carbonyl complexes using microwave hating: demonstrating the use of a gas-loading accessory and real-time reaction monitoring by means of a digital camera. *Organometallics*, **2008**, *27*, 1254-1258.

[76] Tardiff, B. J.; Decken, A.; McGrady, G. S. Microwave-assisted synthesis of $[Os_2Cl_3(PEt_2Ph)_6]Cl$, featuring the first reported X-ray crystal structure. *Inorg. Chem.Commun.*, **2008**, *11*, 44-46.

[77] Jung, J. Y.; Newton, B. S.; Tonkin, M. L.; Powell, C. B.; Powell, G. L. Efficient microwave syntheses of the compounds $Os_3(CO)_{11}L$, L = NCMe, Py, PPh_3. *J. Organomet. Chem.*, **2009**, *694*, 3526-3528.

[78] Harcourt, E. M.; Yonis, S. R.; Lynch, D. E.; Hamilton, D. G. Microwave-assisted synthesis of cyclopentadienyl-cobalt sandwich complexes from diaryl acetylenes. *Organometallics*, **2008**, *27*, 1653-1656.

[79] Tan, N. Y.; Xiao, X. M.; Li, Z. L.; Matsumura-Inoue, T. Microwave synthesis, characterization and DNA-binding properties of a new cobalt(II) complex with 2,6-bis(benzimidazol-2-yl)pyridine. *Chin. Chem. Lett.*, **2004**, *15*, 687-690.

[80] Murugavel, R.; Davis, P.; Walawalkar, M. G. First examples of metal cyclohexylphosphonates: influence of the choice of synthetic route on the product. *Z. Anorg. Allg. Chem.*, **2005**, *631*, 2806-2811.

[81] Amarante, D.; Cherian, C.; Emmel, C.; Chen, H.-Y.; Dayal, S.; Koshy, M.; Megehee, E. G. Improved synthetic routes to rhodium bipyridine complexes: comparison of microwave vs. conventional synthesis. *Inorg. Chim. Acta*, **2005**, *358*, 2231-2238.

[82] Pruszyński, M.; Bilewicz, A.; Zalutsky, M. Preparation of $Rh[16aneS_4\text{-}diol]^{211}At$ and $Ir[16aneS_4\text{-}diol]^{211}At$ complexes as potential precursors for astatine radiopharmaceuticals. Part I: synthesis. *Bioconjug. Chem.*, **2008**, *19*, 958-965.

[83] Yoshikawa, N.; Sakamoto, J.; Matsumura-Inoue, T.; Takashima, H.; Tsukahara, K.; Kanehisa, N.; Kai, Y. Electrochemical and phosphorescent properties of new Ir(III) complexes coordinated by various bipyridine derivatives. *Anal. Sci.*, **2004**, *20*, 711-716.

[84] Yoshikawa, N.; Matsumura-Inoue, T. Electrochemical and phosphorescent properties of new mixed-ligand Ir(III) complexes coordinated with both terpyridine and various bipyridine derivatives. *Anal. Sci.*, **2003**, *19*, 761-765.

[85] Yoshikawa, N.; Yamabe, S.; Kanehisa, N.; Kai, Y.; Takashima, H.; Tsukahara, K. Synthesis, Characterization, and DFT investigation of Ir^{III} tolylterpyridine complexes. *Eur. J. Inorg. Chem.*, **2007**, *13*, 1911-1919.

[86] Konno, H.; Sasaki, Y. Selective one-pot synthesis of facial tris-ortho-metalated iridium(III) complexes using microwave irradiation. *Chem. Lett.*, **2003**, *32*, 252-253.

[87] Saito, K.; Matsusue, N.; Kanno, H.; Hamada, Y.; Takahashi, H.; Matsumura, T. Microwave synthesis of iridium(III) complexes: synthesis of highly efficient orange emitters in organic light-emitting devices. *Jpn. J. Appl. Phys.*, **2004**, *43*, 2733-2734.

[88] Barghurst, D. R.; Cooper, S. R.; Greene, D. L.; Mingos, D. M. P.; Reynolds, S. M. Application of microwave dielectric loss heating effects for the rapid and convenient synthesis of coordination compounds. *Polyhedron*, **1990**, *9*, 893-895.

[89] Buslaeva, T. M.; Kravchenko, V. V.; Kopylova, E. V.; Kashiricheva, I. I.; Alekseeva, O. A.; Kazantsev, S. S. Synthesis and structure of iridium complex with thiocarbamide. *Crystallogr. Rep.*, **2008**, *53*, 775-780.

[90] Zhang, S.-H.; Tang, M.-F.; Ge, C.-M. Microwave synthesis, crystal structure and magnetic behavior of a Schiff base trinuclear nickel cluster. *Z. Anorg. Allg. Chem.*, **2009**, *635*, 1442-1446.

[91] Castan, P.; Labiad, B.; Villemin, D.; Wimmer, F. L.; Wimmer, S. Solid-state cyclometallation of the 1-methyl-2,4'-bipyridinium complexes of palladium$^{\text{II}}$ and platinum$^{\text{II}}$. *J. Organomet. Chem.*, **1994**, *479*, 153-157.

[92] Gosiewska, S.; Herreras, S. M.; Lutz, M.; Spek, A. L.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G.; Klein Gebbink, R. J. M. Synthesis, structure, and catalytic performance of diasteropure five-coordinated NCN-pincer palladium(II) complexes bearing bulky amino acid substituents. *Organometallics*, **2008**, *27*, 2549-2559.

[93] Tu, T.; Malineni, J.; Dötz, K. H. A novel pyridine-bridged bis-benzimidazolylidene pincer palladium complex: synthesis and catalytic properties. *Adv. Synth. Catal.*, **2008**, *350*, 1791-1795.

[94] Shoemaker, K. A.; Leadbeater, N. E. A fast and easy approach to the synthesis of Zeise's salt using microwave heating. *Inorg. Chem. Commun.*, **2009**, *12*, 341-342.

[95] Januário-Charmier, M. A.; Kukushkin, V. Yu.; Pomberio, A. J. L. Microwave-assisted [2 + 3] cycloaddition of nitrones to platinum-(II) and –(IV) bound organonitriles. *Dalton Trans.*, **2003**, 2540-2543.

[96] Desai, B.; Danks, T. N.; Wagner, G. Ligand discrimination in the reaction of nitrones with [PtCl$_2$(PhCN)$_2$]. Selective formation of mono-oxadiazoline and mixed bis-oxadiazoline complexes under thermal and microwave conditions. *Dalton Trans.*, **2004**, 166-171.

[97] Lasri, J.; Januário-Charmier, M. A.; Haukka, M.; Pombeiro, A. J. L. Stereospecific synthesis of polysubstituted *E*-olefins by reaction of acyclic nitrones with free and platinum(II) coordinated organonitriles. *J. Org. Chem.*, **2006**, *72*, 750-755.

[98] Lasri, J.; Januário-Charmier, M. A.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. Direct synthesis of (imine)platinum(II) complexes by iminoacylation of ketoximes with activated organonitrile ligands. *Dalton Trans.*, **2006**, 5062-5067.

[99] Mukhopadhyay, S.; Lasri, J.; Januário-Charmier, M. A.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. Microwave synthesis of mono- and bis-tetrazolato complexes *via* 1,3-dipolar cycloaddition of organonitriles with platinum(II)-bound azides. *Dalton Trans.*, **2007**, 5297-5304.

[100] Mukhopadhyay, S.; Lasri, J.; Guedes da Silva, M. F. C.; Januário-Charmier, M. A.; Pombeiro, A. J. L. *Trans*-bis[5-(4-fluorophenyl)tetrazolato] bis(triphenylphosphine)platinum(II). *Acta Cystallogr., Sect. E: Struct. Rep. Online*, **2007**, *E63*, m2656.

[101] Smoleński, P.; Mukhopadhyay, S.; Guedes da Silva, M. F. C.; Januário-Charmier, M. A.; Pombeiro, A. J. L. New water-soluble azido- and derived tetrazolato-platinum(II) complexes with PTA. Easy metal-mediated synthesis and isolation of 5-substituted tetrazoles. *Dalton Trans.*, **2008**, 6546-6555.

[102] Godbert, N.; Pugliese, T.; Aiello, I.; Bellusci, A.; Crispini, A.; Ghedini, M. Efficient, ultrafast, microwave-assisted syntheses of cycloplatinated complexes. *Eur. J. Inorg. Chem.*, **2007**, *32*, 5105-5111.

[103] Lombard, C. K.; Myers, K. L.; Platt, Z. H.; Holland, A. W. Kinetics of reductive elimination from platinum(IV) as a probe for nonthermal effects in microwave-heating reactions. *Organometallics*, **2009**, *28*, 3303-3306.

[104] Carlsson, M.; Eliasson, B. One-pot synthesis of *trans* mono- or diarylalkynyl substituted platinum(II) compounds with tertiary phosphine or phosphite ligands. *Organometallics*, **2006**, *25*, 5500-5502.

[105] Singh, R. V.; Chaudhary, P.; Chauhan, S.; Swami, M. Microwave-assisted synthesis, characterization and biological activities of organotin(IV) complexes with some thio Schiff bases. *Spectrochim. Acta, Part A*, **2009**, *72*, 260-268.

[106] Hegedus, L. S.; Sundermann, M. J.; Dorhout, P. K. Synthesis, complexation, and coordination oligomerization of 1,8-pyrazine-capped 5,12-dioxocyclams. *Inorg. Chem.*, **2003**, *42*, 4346-4354.

[107] Phetmung, H.; Wongsawat, S.; Pakawatchai, C.; Harding, D. J. Microwave synthesis, spectroscopy, thermal analysis and crystal structure of an one-dimensional polymeric $\{[\mathrm{Cu(4,4'\text{-}bipy)(H_2O)_3(SO_4)}]\cdot 2\mathrm{H_2O}\}_n$ complex. *Inorg. Chim. Acta*, **2009**, *362*, 2435-2439.

[108] Carballo, R.; Covelo, B.; Fernández-Hermida, N.; García-Martínez, E.; Lago, A. B.; Vázquez-López, E. M. Anion effect on the construction of copper(II) coordination polymers with the twisted ligand bis(4-pyridylthio)methane. *Polyhedron*, **2008**, *27*, 3247-3254.

[109] Mohanan, K.; Kumari, B. S.; Rijulal, G. Microwave assisted synthesis, spectroscopic, thermal, and antifungal studies of some lanthanide(III) complexes with a heterocyclic bishydrazone. *J. Rare Earths*, **2008**, *26*, 16-21.

[110] Sonnauer, A.; Stock, N. High-throughput and microwave investigation of rare earth phosphonatoethanesulfonates-*Ln*(O$_3$P-C$_2$H$_4$-SO$_3$) (*Ln* = Ho, Er, Tm, Yb, Lu, Y). *J. Solid State Chem.*, **2008**, *181*, 3065-3070.

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