Microwave-assisted Synthesis of Coordination and Organometallic Compounds

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1. Introduction

Microwave irradiation (MW) as a “non-conventional reaction condition” (Giguere, 1989) has been applied in various areas of chemistry and technology to produce or destroy diverse materials and chemical compounds, as well as to accelerate chemical processes. The advantages of its use are the following (Roussy & Pearce, 1995):

1. Rapid heating is frequently achieved,
2. Energy is accumulated within a material without surface limits,
3. Economy of energy due to the absence of a necessity to heat environment,
4. Electromagnetic heating does not produce pollution,
5. There is no a direct contact between the energy source and the material,
6. Suitability of heating and possibility to be automated.
7. Enhanced yields, substantial elimination of reaction solvents, and facilitation of purification relative to conventional synthesis techniques.
8. This method is appropriate for green chemistry and energy-saving processes.

The substances or materials have different capacity to be heated by microwave irradiation, which depends on the substance nature and its temperature. Generally, chemical reactions are accelerated in microwave fields, as well as those by ultrasonic treatment, although the nature of these two techniques is completely distinct.

Microwave heating (MWH) is widely used to prepare various refractory inorganic compounds and materials (double oxides, nitrides, carbides, semiconductors, glasses, ceramics, etc.) (Ahluwalia, 2007), as well as in organic processes (Oliver Kappe et al, 2009; Leadbeater, 2010): pyrolysis, esterification, and condensation reactions. Recent excellent reviews have described distinct aspects of microwave-assisted synthesis of various types of compounds and materials, in particular organic (Martínez-Palou, 2007; Oliver Kappe et al, 2009; Besson et al, 2006) and organometallic (Shangzhao Shi and Jiann-Yang Hwang, 2003) compounds, polymers, applications in analytical chemistry (Kubrakova, I.V., 2000), among others. Microwave syntheses of coordination and organometallic compounds, discussed in this chapter, are presented by relatively a small number of papers in the available literature in comparison with inorganic and organic synthesis. The use of microwaves in coordination chemistry began not long ago and, due to the highly limited number of results, these works can be considered as a *careful pioneer experimentation*, in order to establish the suitability of this technique for synthetic coordination chemistry. Classic ligands, whose numerous

derivatives have been used as precursors for obtaining their metal complexes, are shown in Table 1.

2. Physical principles of microwave irradiation and laboratory equipment

Microwave heating is a physical process where the energy is transferred to the material through electromagnetic waves. Frequencies of microwaves are higher of 500 MHz. It is known that a non-conductive substance can be heated by an electric field, which polarizes its charges without rapid reversion of the electric field. For some given frequencies, the current component, resulting in the phase with electric field, produces a dissipation of the potency within the dielectric material. Due to this effect, a dielectric can be heated through the redistribution of charges under the influence of external electric fields. The potency dissipated within the material depends on the established electric field within the material. This potency is diminished as the electromagnetic field penetrates to the dielectric.

The most common microwave application is that of multimode type which accepts broad range thermal charges with problems of microwave uniformity. The application of multimode type is given in a closed metallic box with dimensions of various wave lengths and which supports a large number of resonance modes in a given range of frequencies. A resonance cavity or heater consists on a metallic compartment that contains a microwave signal with polarization of the electromagnetic field; it has many reflections in preferential directions. The superposition of the incident and reflected waves gives place to a combination of stationary waves. If the configuration of the electric field is precisely known, the material to be treated can be put to a position of electric field maximum for an optimal transference of electromagnetic energy.

Typical microwave equipment consists of a magnetron tube (Fig. 1) (Roussy & Pearce, 1995). Just as other vacuum tubes, the anode has a higher potential with respect to the cathode (source of electrons). So, the electrons are accelerated to the anode in the electric field. The cathode is heated till the high temperature expulse electrons. Generally, the anode is close to earth potential and the cathode has a high negative potential. The difference between the magnetron and other vacuum tubes is that the electron flow passes along a spiral; this route is created by external magnetic field B (Fig. 1). The electron cloud produces resonance cavities several times in its trip to the anode. These cavities work as *Helmholtz* resonators and produce oscillations of fixed frequency, which is determined by the cavity dimensions: small cavities produce higher frequencies, large cavities give smaller frequencies. The antenna in the right zone collects the oscillations.

Fig. 1. Scheme of microwave equipment.

Fig. 2. Reactor for batchwise organic synthesis (with permission): 1, reaction vessel; 2, top flange; 3, cold finger; 4, pressure meter; 5, magnetron; 6, forward/reverse power meters; 7, magnetron power supply; 8, magnetic stirrer; 9, computer; 10, optic fiber thermometer; 11, load matching device; 12, waveguide; 13, multimodal cavity (applicator).

The use of a microwave reactor for batchwise organic synthesis (Raner et al, 1995), described in Fig. 2), permits to carry out synthetic works or kinetic studies on the 20-100 mL scale, with upper operating limits of 260°C and 10 MPa (100 atm). Microwave-assisted organic reactions can be conducted safely and conveniently, for lengthy periods when required, and in volatile organic solvents. The use of water as a solvent is also explored.

A typical reactor used for organic and/or organometallic syntheses (Matsumura-Inoue et al, 1994) is presented in Fig. 3, which can be easily implemented using a domestic microwave

Fig. 3. Typical MW-reactor for organic and/or organometallic synthesis. With permission.

Fig. 4. Microwave reactors for chemical syntheses. **A:** Emrys Liberator (Biotage, Sweden, www.biotage.com); **B:** CEM Discover BenchMate (CEM, USA, www.cem.com) Copyright CEM Corporation; **C:** Milestone Ethos TouchControl (Milestone, Italy, www.milestonesci.com); **D:** Lambda MicroCure2100 BatchSystem (Lambda, USA, www.microcure.com). With permission.

oven. Due to some problems occurring during microwave treatment, for example, related with the use of volatile liquids (they need of an external cooling system *via* copper ports), original solutions to these problems are frequently found in the reported literature. More modern laboratory MW-reactors (Wiesbrock et al, 2004) are shown in Fig. 4.

A combination of different techniques can frequently improve yields of final compounds or synthetic conditions. Reunion of microwave and ultrasonic treatment was an aim to construct an original microwave-ultrasound reactor (Chemat et al, 1996) suitable for organic synthesis (pyrolysis and esterification) (Fig. 5). The ultrasound (US) system is a cup horn type; the emission of ultrasound waves is made at the bottom of the reactor. The US probe is not in direct contact with the reactive mixture. It is placed a distance from the electromagnetic field in order to avoid interactions and short circuits. The propagation of the US waves into the reactor is made by means of decalin introduced into the double jacket. This liquid was chosen because of its low viscosity that induces good propagation of US and its inertia towards MW.

Some years ago, an alternative method for performing microwave-assisted organic reactions, termed "Enhanced Microwave Synthesis" (EMS), has been examined in an excellent review (Hayes, 2004). By externally cooling the reaction vessel with compressed air, while simultaneously administering microwave irradiation, more energy can be directly applied to the reaction mixture. In "Conventional Microwave Synthesis" (CMS), the initial microwave power is high, increasing the bulk temperature (TB) to the desired set point very quickly. However, upon reaching this temperature, the microwave power decreases or shuts off completely in order to maintain the desired bulk temperature without exceeding it. When microwave irradiation is off, classical thermal chemistry takes over, losing the full advantage of microwave-accelerated synthesis. With CMS, microwave irradiation is predominantly used to reach TB faster. Microwave enhancement of chemical reactions will only take place during application of microwave energy. This source of energy will directly activate the molecules in a chemical reaction. EMS ensures that a high, constant level of microwave energy is applied.

Fig. 5. Combined MW-US reactor. With permission.

3. Complexes with O-containing ligands

3.1 β -Diketonates, alkoxides and alcohol adducts

The MWH of metal β -diketonates or their precursors, represented by acetylacetonates, has been used both for their synthesis (rarely) and destruction (mainly), leading, in the last case, to various inorganic materials, nanostructures and nanocomposites. *Synthesis route* is represented by only a few examples. Thus, a rapid and environmentally benign method for the coupling of 2-naphthols is described using copper(II) acetylacetonate under microwave irradiation in dry media (Meshram et al, 2003). The procedure was found to be very convenient and avoids the use of excess solvent for reaction. Microwave synthesis method was developed for the synthesis of a series of cyclometalated platinum complexes with long chain β -diketone ancillary ligands, with which reaction time was greatly reduced from 32 h to several minutes (Luo et al, 2007; Luo et al, 2007). The formed compounds were used for fabrication of organic light-emitting diodes. A protected ethynyl group was introduced into a γ -position of a (β -diketonato)*bis*(bipyridine)ruthenium(II) complex through the reaction of the bromo complex and (triisopropylsilyl)-acetylene with very good yield under MWH (Munery et al, 2008). Two mononuclear mixed-ligand ruthenium(II) complexes with bipyridine (bpy) and functionalized acetylacetonate ion (acac⁻), [Ru(bpd)(bpy)₂](PF₆) (bpy = 2,2'-bipyridine, bpd = 3-Bromo-2,4-pentanedionate ion) and [Ru(tipsepd)(bpy)₂](PF₆) {tipsepd = 3-((triisopropylsilyl)ethynyl)-2,4-pentanedionate ion} were then prepared as candidates for building blocks. Also, microwave-assisted synthesis method enabled the preparation of the (tris-acetylacetonate)(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) terbium(III) {Tb(acac)₃(dmdpphen)} complex with outstanding high green luminescence and

good thermal stability (Nakashima et al, 2008). This complex was expected to be used in functional materials for electronic products. Zirconium acetylacetonate, $\text{Zr}(\text{acac})_4$, was prepared from its hydrate $\text{Zr}(\text{acac})_4 \cdot 10\text{H}_2\text{O}$ by microwave dehydration of the latter (Berdonosov et al, 1992). Additionally, a convenient method for ^{68}Ga -labeling under anhydrous conditions using solid-phase derived gallium-68-acetylacetonate $\{[^{68}\text{Ga}]\text{Ga}(\text{acac})_3\}$ in a microwave-enhanced radiosynthesis was offered (Zoller et al, 2010). ^{68}Ga was absorbed quantitatively in a cation exchange resin; more than 95% of the generator-eluted ^{68}Ga was obtained from the cation exchange resin with a 98% acetone/2% acetylacetonate mixture providing $[^{68}\text{Ga}]\text{Ga}(\text{acac})_3$ as labeling agent for further use in labeling porphyrin derivatives (^{68}Ga -labeled porphyrins may facilitate the medical application for molecular imaging via positron emission tomography).

MW-decomposition of metal acetylacetonates is represented much more frequently. Thus, silicalite (Si-MFI) zeolite crystals with incorporated tetravalent metal ions were used to MW-synthesize metallosilicalite (M-MFI; $\text{M} = \text{Sn}, \text{Zr}, \text{Sn/Zr}, \text{Ti/Zr}$) zeolites crystals (Hwang et al, 2006). Acetylacetonates were applied as chelating ligands of the metal precursors, to reduce their hydrolysis rates and, therefore, to enhance framework incorporation of each metal in the syntheses of M-MFI zeolites. The resulting zeolite crystals formed showed puck-like morphology and were stacked to form fibers with the degree of self-assembly varied depending on the nature of the tetravalent metal ion used. Chromium-substituted β -diketonate complexes of aluminum were synthesized and employed as precursors for a "soft chemical" process, wherein MWH of a solution of the complex yielded, within minutes, well-crystallized needles of α -($\text{Al}_{1-x}\text{Cr}_x$) $_2\text{O}_3$ measuring 20-30 nm in diameter and 50 nm long (Gairola et al, 2009). By varying the microwave irradiation parameters and using a surfactant such as polyvinyl pyrrolidone, the crystallite size and shape can be controlled and their agglomeration prevented. Mg-Al hydrotalcite-like compounds $\{\text{HT}, \text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})\}$ were prepared by the microwave method with ethoxide-acetylacetonate or acetylacetonate as precursors (Paredes et al, 2006; Paredes et al, 2006). Hydrotalcites prepared with ethoxide-acetylacetonate were found to be better sorbents for $^{131}\text{I}^-$ than those with acetylacetonate. Also, it was established that organic residues presented in the samples prepared by the microwave method favored the sorption of radioactive anions, in particular $^{131}\text{I}^-$ if compared with nitrate and/or carbonate interlayered hydrotalcites. Ferric acetylacetonate, among other iron salts, was used as a precursor to obtain black magnetic Fe_3O_4 nanoparticles in polyhydric alcohols in presence of surfactants (polyethylene glycol, cetyltrimethylammonium bromide, sodium dodecyl benzene sulfonate, etc.) and cosolvents (ethylenediamine, formamide, 1,4-butanediamine and/or butanolamine) (Gao et al, 2009). The product can be used in biomedical, mechanic or electronic fields with strong magnetism, controllable size, and good dispersibility. Additionally, as described in a related work (Bilecka et al, 2008), highly crystalline metal oxide nanoparticles such as CoO , ZnO , Fe_3O_4 , MnO , Mn_3O_4 , and BaTiO_3 were synthesized in just a few minutes by reacting metal alkoxides, acetates or acetylacetonates with benzyl alcohol under microwave heating. At last, organically dispersible nanoalloys were prepared from mixture of salts and metal acetates/acetylacetonates in oleyamine (OAm) and oleic acid (OA), for instance $\text{Pd}(\text{acac})_2\text{-Ni}(\text{HCO}_2)_2\text{-OAm-OA}$ (nanoalloy PdNi) or $\text{Ag}(\text{ac})\text{-Cu}(\text{ac})_2\text{-OAm-OAc}$ (AgCu) (Abdelsayed et al, 2009). High activity and thermal stability have been observed for the nanoalloys according to the order $\text{CuPd} > \text{CuRh} > \text{AuPd} > \text{AuRh} > \text{PtRh} > \text{PdRh} > \text{AuPt}$.

CVD techniques have been successfully applied to decompose metal complexes, in particular microwave plasma aerosol-assisted chemical vapor deposition (MWAACVD), which was used, among other varieties of AACVD, to prepare Y_2O_3 stabilized ZrO_2 , Y_2O_3 doped CeO_2 , Gd_2O_3 doped CeO_2 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ thin films on various ceramic substrates starting from β -diketonate chelates as the source materials (Meng et al, 2004). Amorphous GaF_3 and GaF_3 - BaF_2 thin films were synthesized by electron cyclotron resonance microwave plasma-enhanced CVD (MWPECVD) using metal β -diketonates and a NF_3 gas as starting materials and a fluorinating reagent, respectively (Takahashi et al, 2003). A thin zirconia electrolyte film for a solid oxide fuel cell was prepared on a porous Al_2O_3 substrate by MPECVD using two zirconia sources: zirconium acetylacetonate and zirconium tetra-*n*-butylate (Okamura et al, 2003). As-deposited electrolyte film grown indicated the columnar structure, but this was deformed to a crystal structure with a large crack or pore occurred at grain boundary in film by annealing at 400°C . Additionally, MWPECVD was shown to be a promising method for the solvent free preparation of catalytic materials (Dittmar & Herein, 2009), such as, for example catalytic active chromia species on zirconia and lanthanum doped zirconia supports. During this process, the adsorption of $\text{Cr}(\text{acac})_3$ probably took place by cleavage of one ligand on both supports. Furthermore, the utilization of the PECVD method can inhibit the formation of large CrO_x agglomerates or α - Cr_2O_3 on both supports and, after upscaling, this method can be used for the preparation of catalysts for fine chemicals in larger scale. In a related work (Dittmar et al, 2004), where cobalt oxide supported on titania, $\text{CoO}_x/\text{TiO}_2$, was obtained starting from cobalt(III) acetylacetonate, $\text{Co}(\text{acac})_3$, (precursor) and TiO_2 (support), the $\text{Co}(\text{acac})_3$ was evaporated and adsorbed on carrier surface in a first step and afterwards decomposed during the microwave-plasma treatment in oxygen atmosphere. Volatile copper(II) acetylacetonate was used for preparation of copper thin films in Ar-H_2 atmosphere at ambient temperature by MWPECVD (Pelletier et al, 1991). The formed pure copper films with a resistance of $2\text{--}3\ \mu\Omega\text{cm}$ were deposited on Si substrates. It was noted that oxygen atoms were never detected in the deposited material since Cu-O intramolecular bonds were totally broken by microwave plasma-assistant decomposition of the copper complex.

Additionally to the examples described above on the use of β -diketonate-alkoxide mixtures, *alkoxides* themselves were also reported as precursors for MW-obtaining of inorganic films and structures. Thus, synthesis of TiO_2 and V-doped TiO_2 thin layers was significantly improved and extended under application of microwave energy during the drying and/or calcination step (Zabova et al, 2009). Thin nanoparticulate titania layers were prepared via the sol-gel method using titanium *n*-butoxide as a precursor. The photocatalytic activities of prepared layers were quantified by the decoloring rate of Rhodamine B.

Another type of coordination compounds, molecular *adducts of alcohols* of the composition $\text{VOPO}_4\text{C}_n\text{H}_{2n+1}\text{OH}$ (1-alkanols, $n=1\text{--}18$) and $\text{VOPO}_4\text{C}_n\text{H}_{2n}(\text{OH})_2$ (1, ω -alkanediols, $n=2\text{--}10$) were prepared long ago (Beneš et al, 1997) by the direct reaction of various liquid alcohols with solid and finely ground $\text{VOPO}_4\cdot 2\text{H}_2\text{O}$ in a MW field. According to X-ray diffraction data, the structures of all these polycrystalline complexes retained the original layers of $(\text{VOPO}_4)_\infty$. Alcohol molecules were placed between the host layers in a bimolecular way, being anchored to them by donor-acceptor bonds between the oxygen atom of an OH group and a vanadium atom as well as by hydrogen bonds. Other adducts, $[(n\text{-Bu})_4\text{N}][\text{TMS}_4\text{M}]$ ($\text{M}=\text{Mo}, \text{W}$), were also prepared in the conditions of microwave treatment and their nonlinear optical properties were studied (Lang et al, 1996).

3.2 Carboxylates

MW-synthesized carboxylates are represented mainly by aromatic derivatives possessing multiple carboxylic groups. These complexes are sometimes isolated as adducts with stabilizing ligands as 2,2'-bipy or 1,10-phen, as well as solvent molecules. Thus, by treating $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with a V-shaped ligand 4,4'-oxydibenzoic acid (H_2oba), a dynamic metal-carboxylate framework $[\text{Cu}_2(\text{oba})_2(\text{DMF})_2] \cdot 5.25\text{DMF}$ (MCF-23; DMF = N,N-dimethylformamide) was synthesized, which features a wavelike layer with rhombic grids based on the paddle-wheel secondary building units (Wang et al, 2008). These layers stack *via* strong offset π - π stacking of the Ph groups of oba ligands to give 3D porosity. A MWAS solvothermal method was proven to be a faster and greener approach to synthesize phase-pure MCF-23 in high yield without impurities, typical for conventional synthesis. In contrast, the product obtained by the conventional solvothermal method was not phase-pure. Two isostructural coordination polymers, $\text{M}_3(\text{NDC})_3(\text{DMF})_4$ ($\text{M} = \text{Co}, \text{Mn}$; $\text{H}_2\text{NDC} = 2,6\text{-naphthalenedicarboxylic acid}$), crystallizing in the monoclinic system with space group C2/c, were prepared through conventional and MWAS solvothermal methods (Liu et al, 2008). These microporous cobalt(II) and manganese(II) coordination polymers underwent reversible structural change upon desolvating, giving stable microporous frameworks containing unsaturated metal sites.

Trimesic acid **1** and its analogue, containing four carboxylate units, have been reported in a series of publications related to MWAS of metal complexes. Thus, two isostructural coordination polymers $(\text{EMim})_2[\text{M}_3(\text{TMA})_2(\text{OAc})_2]$ ($\text{M} = \text{Ni}$ or Co , EMim = 1-ethyl-3-methylimidazolium, $\text{H}_3\text{TMA} = \text{trimesic acid}$) with anionic metal-organic frameworks were synthesized under microwave conditions using an ionic liquid EMIm-Br as solvent and template (Lin et al, 2006). In a related report, the microwave solvothermal reaction of nickel nitrate with trimesic acid provided the $[\text{Ni}_3(\text{BTC})_2(\text{H}_2\text{O})_{12}]_n$ (BTC = benzene-1,3,5-tricarboxylate anion of trimesic acid), which is a metal coordination polymer composed of 1D zigzag chains (Hsu et al, 2009). In the asymmetric unit, two types of Ni atoms were found: one of the NiO_6 groups was coordinated to only one carboxylate group and thus terminal, the other is bridging, forming the coordination polymer. Magnesium coordination polymers, $[\text{Mg}_2(\text{BTEC})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, $[\text{Mg}_2(\text{BTEC})(\text{H}_2\text{O})_6]$, and $[\text{Mg}_2(\text{BTEC})(\text{H}_2\text{O})_8]$ (BTEC = 1,2,4,5-benzenetetracarboxylate anion), were synthesized from magnesium nitrate and 1,2,4,5-benzenetetracarboxylic acid with variable ratios of organic base under MW solvothermal reactions at 150-180°C (Liu et al, 2009). Structure of MW-synthesized complex $\{[\text{Co}_2(\text{C}_2\text{O}_4)(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})]_4 \cdot 4\text{H}_2\text{O} \cdot (\text{NH}_2\text{CH}_2\text{COOH})\}_n$ (crystallized in the monoclinic system and the space group Cc), had a flattened octahedral configuration (Xu & Fan, 2007). Three mixed-ligand cobalt(II) complexes $[\text{Na}_2\text{Co}(\mu_4\text{-btec})(\text{H}_2\text{O})_8]_n$, $[\text{Co}_2(\mu_2\text{-btec})(\text{bipy})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$, and $[\text{Co}_2(\mu_2\text{-btec})(\text{phen})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ ($\text{H}_4\text{btec} = 1,2,4,5\text{-benzenetetracarboxylic acid}$, bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline) were synthesized using hydrothermal and microwave methods (Shi et al, 2009). All three complexes were found to be bridged by the ligands to form 3D (first complex) and binuclear (other complexes) structures.

Three isostructural 2D metal-organic frameworks, $[\text{M}(\text{bpydc})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]_n$ (where $\text{M} = \text{Zn}$; Co ; Ni and bpydc is 2,2'-bipyridine-5,5'-dicarboxylate), were prepared by hydrothermal, ultrasonic and MWAS methods (Huh et al, 2010). The coordination environment of the metal ions was found to be a distorted octahedral geometry. The metal ions were found to be coordinated by two nitrogen atoms from the bipyridyl moiety, two oxygen atoms from one

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carboxylate in a bidentate manner, one oxygen atom from another carboxylate in a monodentate manner, and one oxygen atom from the aqua ligand. $[\text{Zn}(\text{bpydc})(\text{H}_2\text{O})\cdot\text{H}_2\text{O}]_n$ displayed strong solid state blue luminescence. Additionally, the green synthesis of a variety of 3,4-disubstituted-1-H-pyrrole-2-carboxylates was described (Dickhoff et al, 2006).

As an example of MW-decomposition of metal carboxylates leading to nanostructures, Ni nanoparticles with average sizes of 43, 71, and 106 nm were obtained by the intramolecular reduction of Ni^{2+} ion contained in a formate complex having long-chain amine ligands {oleylamine (=Z)-9-octadecenylamine), myristylamine (=tetradecylamine), and laurylamine (=dodecylamine)} within an extremely short time under MW conditions (Yamauchi et al, 2009). Formate ion coordinated to Ni^{2+} ion acted as a reducing agent for Ni^{2+} in this reaction and finally decomposed to hydrogen and carbon dioxide. Also, microwave synthesis of metal oxide nanoparticles, $\gamma\text{-Fe}_2\text{O}_3$, NiO, ZnO, CuO and Co- $\gamma\text{-Fe}_2\text{O}_3$ were carried out by microwave-assisted route through the thermal decomposition of their respective metal oxalate precursors employing polyvinyl alcohol as a fuel (Lagashettya et al, 2007).

3.3 Nitrogen-containing ligands

N-Containing ligands are widely represented (although lesser in comparison with N,O-ligands) by substituted derivatives of classic heterocycles with 1÷3 nitrogen atoms (Table 1), such as azoles, azines (in particular polypyridines), frequently together with carboxylate anions (see also the section on N,O-containing ligands) or CO-groups. Thus, among *azole complexes*, MWAS of the neutral complex *fac*- $[\text{ReL}(\text{CO})_3\text{Cl}]$ and isomers thereof were carried out by reacting the chelating ligand 4-[4,6-*bis*(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazin-2-yl]-N,N-diethyl-benzenamine, L, with pentacarbonylchlororhenium in toluene (Salazar et al, 2009). Further substitution of the carbonyl and/or the chloride attained multiple products with remarkable luminescence properties that included thermochromism, rigidochromism, solvatochromism, and/or vapochromism. Cobalt(II) pyrazolate metal-organic frameworks comprising bridging *bis*-pyrazolyl ligands $(3,5\text{-R}_{1,2}\text{C}_3\text{HN}_2)\text{-(}1,4\text{-C}_6\text{H}_3\text{R}_2\text{)}_n\text{-(}3,5\text{-R}_{1,2}\text{C}_3\text{HN}_2)$ ($\text{C}_3\text{H}_3\text{N}_2 = 1\text{H-pyrazol-4-yl}$; $n = 0\text{-}3$, $\text{R}^1, \text{R}^2 = \text{H, halo, CF}_3, \text{OH, NH}_2, \text{CHO, C}_{1\text{-}6}\text{ alkyl, alkenyl, alkynyl, alkoxy}$), tetrahedrally coordinated to Co(II) ions, useful as redox-active materials, oxidation catalysts, adsorbents and storage materials for H_2 and methane, gas sensors, were prepared by conventional or MWH of solutions containing Co(II) salts with F^- , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , AcO^- anions, and the bis-pyrazolyl ligands above in water, MeOH, EtOH, DMF, N,N-diethylformamide, PhCl, N-methylpyrrolidone at 80-140°C for 1-150 h (Bahnmüller et al, 2009). The complex $[\text{ReO}_3\{\mu_3\text{-SO}_3\text{C}(\text{pyz})_3\}]$ **2** was prepared in 42% yield by reacting lithium *tris*(1-pyrazolyl)methanesulfonate with rhenium(VII) oxide in water at ambient temperature during 5 h (or 30 min under microwave irradiation at 20°C) (Pombeiro et al,

2007). These complexes were used as catalysts in the following reactions: a) partial oxidation of ethane into acetic acid or its carboxylation into propionic acid in the atmosphere of CO; b) partial oxidation of ethane into acetaldehyde; c) partial peroxidative oxidation of cyclohexane into cyclohexanol and cyclohexanone.

Benzimidazole complexes have also been MW-prepared. Thus, a cobalt(II) complex, $[\text{Co}(\text{H}_2\text{bzimpy})_2](\text{ClO}_4)_2$, with tridentate ligand 2,6-*bis*(benzimidazol-2-yl)pyridine (H_2bzimpy) was synthesized by microwave irradiation method (Tan et al, 2004). The *bis*(2-benzimidazolylmethyl)amine was synthesized under the microwave irradiation, and the complex $[\text{DyL}_2(\text{NO}_3)_2\text{NO}_3]$ {where L is *bis*(2-benzimidazolylmethyl)amine} was synthesized (Ouyang et al, 2009). The dysprosium (III) complex was found to bind to DNA base pairs by partial intercalation and electrostatic binding. Additionally, pincer-type, pyridine-bridged *bis*(benzimidazolylidene)-palladium complexes **3** ($\text{R} = n\text{-C}_{16}\text{H}_{33}$, $\text{X} = \text{Br}$; $\text{R} = n\text{-C}_{16}\text{H}_{33}$, $\text{X} = \text{I}$; $\text{R} = n\text{-C}_8\text{H}_{17}$, $\text{X} = \text{I}$; $\text{R} = n\text{-C}_4\text{H}_9$, $\text{X} = \text{I}$) were synthesized from cheap commercial precursors under microwave assistance

Among *azine metallocomplexes*, cyclometalated chloroplatinum complexes containing neutral monodentate ligands such as 2-phenylpyridine, 2-(2'-thienyl)pyridine or 4-

methoxypyridine, as well as the cyclometalated benzo[h]quinoline chloride complex with 4-methoxypyridine, were synthesized in a few minutes in 63-99% yields by irradiating the reaction mixture with microwaves (Godbert et al, 2007). The availability of this class of complexes in a few minutes offers the possibility of a combinatorial approach for the preparation of libraries of homologous compounds of potential interest for large-scale screening studies. MWAS of $[\text{Cu}_2(\text{pz})_2(\text{SO}_4)(\text{H}_2\text{O})_2]_n$ (pz = pyrazine) produced monocrystal suitable for X-ray diffraction studies, reducing reaction time and with higher yield than the classical hydrothermal procedures (Amo-Ochoa et al, 2007). The iridium complexes, obtained by cyclometalation of 5-(3-cyanophenyl)-2,3-diphenylpyrazine by 0.22 g of $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ in 2-ethoxyethanol under a 100 W MW for 30 min, featured emission at 632 nm in chloroform solution, by reaction with sodium acetylacetonate (Inoue & Seo, 2010). The products were found to be useful as a phosphorescent compound for use in organic light-emitting devices. MWAS of the ligands *bis*(2-pyridylmethyl)amine (BMPA), Me 3-[*bis*(2-pyridylmethyl)amino]propanoate (MPBMPA), 3-[*bis*(2-pyridylmethyl)amino]propanamide (PABMPA), 3-[*bis*(2-pyridylmethyl)amino]propionitrile (PNBMPA), (3-aminopropyl)*bis*(2-pyridylmethyl)amine (APBMPA), and lithium 3-[*bis*(2-pyridylmethyl)amino]propanoate (LiPBMPA) were reported (Pimentel et al, 2007). A series of 2-(1-alkyl/aryl-1H-1,2,3-triazol-4-yl)pyridine (pytrz) ligands were synthesized using microwave-assisted Huisgen-Meldal-Fokin 1,3-dipolar cycloaddition and were used to prepare homoleptic and heteroleptic ruthenium(II) complexes with 4,4'-dimethyl-2,2'-bipyridine as second ligand (Happ, 2009). The iridium-quinoxaline complex **4** (where X is H or F) was prepared from iridium trichloride hydrate as metal source precursor in ethylene glycol by MWH for 4-5 min (Zhang et al, 2008). The complex had high solubility in common organic solvents, and can be used as electrophosphorescent material with high luminescence efficiency.

Complexes of such classic *polypyridine ligands* as 2,2'- or 4,4'-bipyridine (bipy) {or closely related 1,10-phenanthroline (phen), which in terms of its coordination properties is similar to 2,2'-bipyridine} and their derivatives were also prepared by MWH, for instance $[\text{Co}(\text{phen})_2\text{Cl}_2]\text{ClO}_4$ (Jin et al, 2009). A metal organic-inorganic coordination framework formulated as $\{[\text{Cu}(4,4'\text{-bipy})(\text{H}_2\text{O})_3(\text{SO}_4)] \cdot 2\text{H}_2\text{O}\}_n$ were similarly synthesized (Phetmung et al, 2009). The resulting compound was an 1D polymer in which 4,4'-bipy acted as a bridging ligand supporting the formation of infinite $[\text{Cu}(4,4'\text{-bipy})(\text{H}_2\text{O})_3(\text{SO}_4)]$ chains. Several

reports are dedicated to noble metals, in particular ruthenium complexes; thus, microwave mediated reaction of $[\text{Ru}(\text{COD})\text{Cl}_2]_n$ with 4,4'-di-*tert*-butyl-2,2'-bipyridine (tbbpy) in DMF gave 97.5% $\text{Ru}(\text{tbbpy})_2\text{Cl}_2$ which on treatment with 5,5',6,6'-tetramethyl-2,2'-bibenzimidazole (tmbibim)/ NH_4PF_6 gave 63% $[\text{Ru}(\text{tbbpy})_2(\text{tmbibim})](\text{PF}_6)_2$ (Walther et al, 2005). Ruthenium(II) polypyridine complex $[\text{Ru}(\text{Hdpa})_3](\text{ClO}_4)_2$ {Hdpa = *bis*(2-pyridyl)amine} was prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in a few minutes in 91% yield (Xiao et al, 2002). Poly(bipyridine)ruthenium complexes $[\text{RuCl}_2(\text{dcmb})_2]$ (dcmb = 4,4'-dimethoxycarbonyl-2,2'-bipyridine) and $[\text{Ru}(\text{dcmb})_{3-n}(\text{tbbpy})_n](\text{PF}_6)_2$ ($n = 0-3$ and tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) were also synthesized (Schwalbe et al., 2008). With the same tbbpy ligand, the oxodiperoxo complex $\text{MoO}(\text{O}_2)_2(\text{tbbpy})$ was isolated from the reaction of $\text{MoO}_2\text{Cl}_2(\text{tbbpy})$ in water under MWH at 120°C for 4 h (Amarante, 2009). It was established that the Mo^{VI} centre is seven-coordinated with a geometry which strongly resembles a highly distorted bipyramid. The crystal structure is formed by the close packing of the columnar-stacked complexes. Interactions between neighbouring columns are essentially of van der Waals type mediated by the need to effectively fill the available space. The authors noted that their synthesis route was surprising, since all known standard procedures for the synthesis of this type of complex involved a peroxide source such as H_2O_2 or *tert*-butyl hydroperoxide (TBHP). Rh^{III} complexes $[\text{Ru}(\text{L})_2](\text{PF}_6)_2$ ($\text{L} = \text{L}^1$ or L^2) of enantiomerically pure, chiral terpyridyl-type ligands ligands L^1 ('dipineno'-[5,6:5'',6'']-fused 2,2':6',2''-terpyridine, 2,6-*bis*(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)pyridine) and L^2 ('dipineno'-[4,5:4'',5'']-fused 2,2':6',2''-terpyridine, 2,6-*bis*(7,7-dimethyl-5,6,7,8-tetrahydro-6,8-methanoisoquinolin-3-yl)pyridine), synthesized in high yields starting from 2,6-diacetylpyridine and enantiopure α -pinene, with Rh^{III} and Ru^{II} were prepared (Ziegler et al, 1999) and studied spectroscopically. These complexes had a helically distorted terpyridyl moiety, as shown by the considerable optical activity in the ligand centered and metal to ligand charge transfer transitions. Additionally, the MWAS (from $\text{Bpy}_2\text{OsCl}_2 \cdot 6\text{H}_2\text{O}$ as Os source) and photophysical properties of heterometallic dinuclear complex based on ruthenium and osmium *tris*-bipyridine units, $\text{Ru-mPh}_3\text{-Os}$ (**5**), in which the metal complexes were linked via an oligophenylene bridge centrally connected in the *meta* position, were described (Aléo et al, 2005).

In a difference with acetylacetonates, the N-containing complexes are more rarely applied as precursors using MW-treatment for obtaining metal alloys and nanostructures. Thus, cyanogel coordination polymers (amorphous Prussian blue analogs formed in a hydrogel

state by the reaction of a chlorometalate with a cyanometalate in aqueous solution) can be thermally auto-reduced to form transition-metal alloys {binary and ternary transition-metal alloys (Pd/Co, Pt/Co, Ru/Co, Ir/Co, Pd/Ni, Pt/Ni, Pt/Ru, Pd/Fe, Pd/Fe/Co) and intermetallics (Pt₃Fe, Pt₃Co, PtCo)}, in particular by MWH (Vondrova et al, 2007). The authors showed that the cyanogel polymers are susceptible to microwave dielectric heating, which leads to a sufficient temperature increase in the sample to cause the reduction of the metal centers, thus allowing for the conversion of cyanogels to metal alloys in a few minutes instead of hours needed in the traditional furnace heating.

3.4 Porphyrins

MWAS techniques have been developed for the synthesis and/or rearrangements of both metal-free porphyrins (Yaseen et al, 2009; Hou et al, 2007) and their metal complexes. Thus, several substituted 5,10,15,20-tetraarylporphyrins {5,10,15,20-tetraphenylporphyrin, 5,10,15,20-*tetrakis*(4-chlorophenyl)porphyrin, and 5,10,15,20-*tetrakis*(3-hydroxyphenyl)porphyrin} and insertion of five different transition metals into the porphyrin core were achieved with high yields using MW (Nascimento et al, 2007). Experimental protocols were characterized by extremely short reaction times and quite small quantities of solvents employed. 5,10,15,20-*Tetrakis*(2-pyridyl)porphyrin (H₂TPyP) and its complex, Mn(III)TPyP, were synthesized under MWH in the presence of propionic acid (Zhang et al, 2006). A *tetrakis*(terpyridinyl)porphyrin derivative and its Ru^{II} complexes, obtained through microwave-enhanced synthesis, were found to have photovoltaic properties and nanowire self-assembly (Jeong et al, 2007). Condensation adducts of the Ni(II) and Cu(II) complexes of β -amino-*meso*-tetraphenylporphyrin with di-Me acetylenedicarboxylate (DMAD) and di-ethylethoxymethylenemalonate were converted into the corresponding esters of pyridinone-fused porphyrins by using different cyclization protocols, including MW (Silva et al, 2009), resulting high yields in a short period of time under closed-vessel conditions. Soluble 5,10,15,20-*tetrakis*(4-*tert*-butylphenyl)metalloporphyrins [M(TBP), M = Mg, Cu, Tb(OAc), Lu(OAc), La(OAc)] were rapidly synthesized by microwave irradiation from 5,10,15,20-*tetrakis*(4-*tert*-butylphenyl)porphyrins [H₂(TBP)] or from pyrrole and 4-*tert*-butylbenzaldehyde with appropriate metal salts (Liu et al, 2005). The observed fluorescent properties of metalloporphyrins depend on their central metals due to heavy-atom effect. In a related work, soluble 5,10,15,20-*tetrakis*(4-*tert*-butylphenyl)magnesium porphyrins {Mg(TBP)}, perylene tetracarboxylic derivative [N,N'-bis(1,5-dimethylhexyl)-3,4:9,10-perylenebis(dicarboximide), PDHEP], and porphyrin-perylene tetracarboxylic complex were quickly prepared under MWH (Liu et al, 2004). It was revealed that porphyrin-perylene tetracarboxylic complex exhibited better fluorescent quantum yield and photo-electricity conversion effect than Mg(TBP) and PDHEP, respectively. MWAS methods were also developed to cleanly produce the tetra(2',6'-dimethoxyphenyl)porphyrin and its Fe, Zn, and Ni complexes (Wolfel et al, 2009). Additionally, Cu(II) complexes with asymmetrical (5-(3-hydroxyphenyl)-10,15,20-*tris*-(4-carboxymethylphenyl)-21,23-Cu(II)-porphine) **6** and symmetrical (5,10,15,20-*meso-tetrakis*-(4-carboxymethylphenyl)-21,23-Cu(II) porphine) **7** porphyrinic ligands were synthesized with superior yields using MW to be used in unconventional treatment of various diseases by means of photodynamic therapy (PDT) (Boscencu et al, 2010). The results of the biological *in vitro* tests indicated a low cytotoxicity

of the compounds for the studied cells. At last, the one-step 15 min (instead of 24 h by classic preparation) synthesis of metalloporphyrazines with enhanced yields directly from substituted maleonitriles, involving tetramerization using hexamethyldisilazane and *p*-toluenesulfonic acid and DMF in a sealed tube under MW (Chandrasekharam et al, 2007).

3.5 Phthalocyanines

Phthalocyanine (Pc) area is industrially important, in a difference with major part of N-containing ligands having an academic interest only, since both metal free phthalocyanines and their several metal complexes (Cu, Zn, Ni, Fe, etc.) are produced during several decades in large quantities and used as pigments, in compact disk production, and catalysis, among many other applications. So, novel techniques for their production are permanently in search, as for classic Pcs as for substituted (generally R_4Pc for symmetrical Pcs; R = alkyl, aryl, Cl, NO_2 , ethers, crowns, etc.). In particular, a variety of metal phthalocyanine complexes has been fabricated via MWH allowing absence of solvents (we note that solvent nature is very important for tetramerization of phthalonitrile and other Pc precursors). Thus, metal substituted octachlorophthalocyanines ($M = Fe, Co, Ni, Cu, Zn$), hexadecachlorophthalocyanines ($M = Fe, Co, Ni, Cu$) and tetranitrophthalocyanines ($M = Fe, Co, Ni, Cu, Pd$) were synthesized by exposure to MW under solvent free and reflux conditions (Safari et al, 2004; Shaabani et al, 2003). The synthesis of various axially substituted Ti phthalocyanines in high yield using MW without solvent was reported (Maree, 2005). The times of reaction, as expected, were short (generally <10 min). Substituted Fe and Co octachloro-, tetranitro-, tetracarboxy- or polyphtalocyanines were easily prepared by MWH of the starting materials under solvent free condition, which reduced reaction time considerably and used as epoxidation catalysts of cyclooctene in homogeneous and heterogeneous conditions by iodosylbenzene as an oxidant (Bahadoran & Dialameh, 2005). Their catalytic activities showed that the electron withdrawing groups on the phthalocyanine ring have a very small effect on stability of the catalyst during the reactions. The tetrasubstituted metal-free phthalocyanine **8** ($R = SO_2NH-p-C_6H_4Me$) and its

nickel and zinc metallophthalocyanines bearing four 14-membered tetraaza macrocycles moieties on peripheral positions were synthesized by cyclotetramerization reaction of phthalonitrile derivative **9** in a multi-step reaction sequence (Biyiklioglu et al., 2007). Additionally, a reaction mixture containing perfluoro-phthalonitrile reacted in a vessel with application of microwave energy for a reaction period sufficient to yield a fluorinated phthalocyanine (Fraunhofer-Gesellschaft et al, 2009), having wide ranging applications, e.g., corrosion-related applications, coating-related applications, catalysis, and the production of optical and electronic materials.

Thermal and microwave reactions between $[\text{PcSn}^{\text{IV}}\text{Cl}_2]$ and the potassium salts of eight fatty acids led to *cis*- $[(\text{RCO}_2)_2\text{Sn}^{\text{IV}}\text{Pc}]$ compounds $\{\text{R} = (\text{CH}_2)_n\text{Me} (n = 4, 6, 8, 10, 12, 14, 16) \text{ and } (\text{CH})_7\text{-cis-CH:CH}(\text{CH}_2)_7\text{Me}\}$ in yields ranging from 54 to 90% (Beltran et al, 2005). Some products revealed anticorrosion properties. Triazol-5-one substituted phthalocyanines were prepared quickly by the reactions (*I*) of 4-nitrophthalonitrile with anhydrous metal ($\text{M} = \text{Co}, \text{Cu}, \text{Zn}, \text{Ni}$) salts in DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) and DMAE (dimethylaminoethanol) by MW. Microwave yields were found to be higher than those of the conventional synthesis methods (Kahveci et al, 2006). We note that some metal-free substituted phthalocyanines $\{2,9(10),16(17),23(24)\text{-tetra}(3,5\text{-dimethylphenoxy})\text{ phthalocyanine}, 2,9(10),16(17), 23(24)\text{-tetra}(4\text{-tert-butylphenoxy})\text{ phthalocyanine}, \text{ and } 2,9(10),16(17),23(24)\text{-tetra}(3,5\text{-di-tert-butyl-4-hydroxyphenyl})\text{ phthalocyanine}\}$ were also obtained by similar routes with higher yields in comparison with conventional methods (Seven et al, 2009). These Pc-compounds had high thermal stability, which was determined at 520°C (midpoint), 549°C, and 400°C, respectively, as a maximum weight loss temperature.

Bis- and *sub*-phthalocyanines, as well as mixed phthalocyanine-porphyrin complexes, were also reported as MW-fabricated. Thus, starting with phthalic and 4-*tert*-butylphthalic acid derivatives, the *bis*phthalocyanines of rare earth elements and Hf and Zr were MW-prepared (Kogan et al, 2002). *Sub*-phthalocyanine (SubPc) derivatives with different kind of substituent groups were synthesized from various phthalonitriles using conventional and microwave heating sources (Kim et al, 2009). Compared to the conventional synthesis, it was

found that SubPc derivatives were synthesized in a shorter reaction time with a higher synthetic yield by MW. A soluble phthalocyanine-porphyrin complex {Lu(TBPor)Pc} was quickly obtained by MWH; Lu(TBPor)Pc was shown to have better photoelectric conversion properties than porphyrin {Lu(TBPor)OAc}, phthalocyanine {H₂(TBPC)}, and Lu(TBPor)OAc/H₂(TBPC) blend (Liu et al, 2004). More information on MW-synthesis of phthalocyanines was reported: Ga (Masilela & Nyokong, 2010), and other metals (Co, Ni, Cu, Mg, Al, Pd, Sn, Tb, Lu, Ce, La, Zn) (Hu et al, 2002; Park et al, 2001).

4. Complexes with N,O-containing ligands

These coordination compounds are widely represented by a series of oximes, amines, imines, Schiff bases, as well as such cyclic N,O-ligands as oxadiazoline. Cluster complexes have been also reported, in particular those that cannot be obtained by standard non-microwave techniques. Thus, tetradentate N₂O₂ ligand [HO(Ar)CH:N-(CH₂)₂-N:CH(Ar)OH] (Ar = *o*-C₆H₄) and manganese(II), cobalt(II), nickel(II), and zinc(II) diimine complexes ML were synthesized by classical and MW techniques (Pagadala et al., 2009). It was proposed that, probably, the metal is bonded to the ligand through the phenolic oxygen and the imino nitrogen. The reaction of Ni(ClO₄)₂·6H₂O with 2-hydroxybenzaldehyde and an aqueous solution of methylamine in acetonitrile/MeOH under MWH and controlled temperature/pressure gave trinuclear cluster [Ni₃(mimp)₅-(MeCN)]ClO₄ (mimp = 2-methyliminomethylphenolate anion) in only 29 min and also resulted in higher yields in contrast to other synthesis methods (Zhang et al, 2009). This complex displayed dominant ferromagnetic interactions through μ₃-O (oxidophenyl) and μ₂-O (oxidophenyl) binding modes. Another cluster, unusual for a specific group of complexes, was found for an oxime complex. Thus, the microwave-assisted reaction of Fe(O₂CMe)₂ with salicylaldoxime (saoH₂) in pyridine produced an octametallic cluster [Fe₈O₄(sao)₈(py)₄] in crystalline form in 2 min (Gass et al, 2006). The core of the complex contained a cube encapsulated in a tetrahedron while sao²⁻ exhibited a unique coordination mode η²:η¹:η¹:μ₃ among the structurally characterized metal complexes containing the sao²⁻ ligand. The authors noted that [Fe₈O₄]⁴⁺ core is uncommon, observed earlier only in one other complex: [Fe₈O₄(pz)₁₂Cl₄] (pz = pyrazolate anion). The MW-heating had not only led to the isolation of a beautiful and unusual {Fe^{III}}₈ cluster, impossible to produce under ambient reaction conditions, but has also greatly improved the reaction rate and enhanced the yield in comparison to solvothermal methods.

Among other oxime complexes, the metal-mediated iminoacylation of *ketoximes* R¹R²C:NOH (R¹ = R² = Me; R¹ = Me, R² = Et; R¹R² = C₄H₈; R¹R² = C₅H₁₀) upon treatment with the platinum(II) complex *trans*-[PtCl₂(NCCH₂CO₂Me)₂] with an organonitrile bearing an acceptor group proceeded under mild conditions in dry CH₂Cl₂ or in microwave field to give the *trans*-[PtCl₂{NH:C(CH₂CO₂Me)ON:CR¹R²}₂] isomers in moderate yield (Lasri et al, 2006). Nine cobaloximes of the type *trans*-[Co(dmgH)₂(B)X], where dmgH⁻ = dimethylglyoximate anion, X⁻ = Cl⁻, Br⁻ or I⁻ and B = pyrazine, Pz (1 to 3), pyrazine carboxylic acid, PzCA (4 to 6), pyrazine carboxamide, PzAM (7 to 9), imidazole (Imi) or histidine (His), were prepared (an example of the complex, N,N'-dihydrogenpiperazonium dichloridobis(dimethylglyoximate-k²N,N')cobaltate(III) dihydrate, PpH₂[Co(dmgH)₂Cl₂]₂·2H₂O, is shown by formula **10**) (Martin et al, 2008; Dayalan et al,

2009). The free ligands Pz, PzCA and PzAM showed antibacterial activity in the order: Pz > PzCA > PzAM whereas, the free equatorial ligand dmgh₂ was inactive against all the bacteria tested. The cobaltoximes were more active than the corresponding pyrazine and its derivatives as axial ligand in the complexes. It was revealed that the bromo complexes dissociated at higher temperatures compared to the chloro complexes, the iodo cobaloximes being unstable even at low temperature decomposing without any sharp change in mass. Iodocobaloximes were found to be more active than the corresponding chloro- and bromo-cobaloximes with the antibacterial activity order for the axial halides as I⁻ > Cl⁻ > Br⁻ and that of the axial nitrogen heterocycles as histidine > imidazole. Additionally, a 3D coordination polymer, [Cd(μ₃-HIDC)(bbi)_{0.5}]_n {H₃IDC = 4,5-imidazoledicarboxylic acid, bbi = 1,1'-(1,4-butanediyl)bis(imidazole)}, was synthesized under MWH solvothermal conditions (Liu et al, 2008). Its crystal structure consisted of 2-D brickwall-like networks of [Cd(μ₃-HIDC)]_n, which are further linked through μ₂-bbi to generate a 3D structure.

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Microwave-assisted [2+3] cycloaddition of nitrones to the nitrile ligands in *cis*- or *trans*-[PtCl₂(PhCN)₂] occurred under ligand differentiation and allowed for selective synthesis of *cis*- or *trans*-[PtCl₂(oxadiazoline)(PhCN)] (Desai et al, 2004). Reaction of the *trans*-substituted mono-oxadiazoline complexes with a nitron different from the one used for the first cycloaddition step gave access to mixed *bis*-oxadiazoline compounds *trans*-[PtCl₂(oxadiazoline-a)(oxadiazoline-b)]. The corresponding *cis*-configured complexes, however, did not undergo further cycloaddition. In case of palladium complexes, the reaction between the nitron *p*-MeC₆H₄CH:N(Me)O and *trans*-[PdCl₂(RCN)₂] (R = Ph, Me) in the corresponding RCN (or of the nitron in neat RCN in the presence of PdCl₂) proceeded at 45°C (R = Ph) or reflux (R = Me) for 1 day and gave the Δ4-1,2,4-oxadiazoline complexes [PdCl₂{Na:C(R)ON(Me)CbH(C₆H₄Me-*p*)₂(Na-Cb)}] (R = Ph, Me) in ~50 and ~15% yields, respectively (Bokach et al, 2005). The reaction time can be drastically reduced by focused MW of the reaction mixture.

Phenylantimony chloride and Sb chloride complexes with Schiff base ligands having N-S and N-O donor systems were synthesized under MW using a domestic microwave oven from hours to a few seconds with improved yield as compared with conventional heating (Mahajan et al, 2008). The treatment with the ligands and their phenylantimony derivatives at dose levels of 20 mg per rat per day did not cause any significant change in body weight, but a significant reduction in the weights of reproductive organs was observed. Transition

metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Hg(II), and Sn(II) were synthesized from the Schiff base (L) derived from 4-aminoantipyrine and 4-fluoro-benzaldehyde using traditional synthetic methodology and microwave-induced organic reaction enhancement (MORE) technique (Ali et al, 2010). Neat reactants were subjected to microwave irradiation giving the required products more quickly and in better yield compared to the classical methodology. As an example of use of Schiff base complexes for catalytic purposes, we note an octahedral titanium binaphthyl-bridged Schiff base complex **11**, investigated in respect of catalytic behavior toward epoxidation of allylic alcohols (Soriente et al, 2005). It was established that a mixture of monoterpene alcohol **12**, *tert*-Bu hydroperoxide, the complex **11**, and CH₂Cl₂, being irradiated with microwave for 15 min, gave 87% terpene epoxy alcohol **13**.

Four ligands *i.e.* N,N'-bis(3-carboxy-1-oxoprop-2-enyl)-1,2-dimethylethylenediamine (CDMPE), N,N'-bis(3-carboxy-1-oxoprop-2-enyl)-1,2-dimethylethylenediamine (CDMPE-2), N,N'-bis(3-carboxy-1-oxoprop-2-enyl)-1,2-diethylethylenediamine (CDEPE), N,N'-bis(3-carboxy-1-oxoprop-2-enyl)-1,2-diethylethylenediamine (CDEPE-2) and their manganese complexes were prepared by microwave method (Bhojak et al, 2008). Antibacterial activity of the ligands and complexes were also reported on *S. aureus* and *E. coli*. Complexes of Mn(II) with 4 amide group containing ligands (Bhojak et al, 2007) {N, N'-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-ethylenediamine (CPE), N,N'-bis-(3-carboxy-1-oxo-prop-2-enyl)-1,2-phenylenediamine (CPP), N,N'-bis-(2-carboxy-1-oxophenelenyl)-1,2-phenylenediamine (CPPP), N,N'-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-phenylenediamine (CPP-2), obtained by MW-heating of amine and carboxylic acid} were MW-synthesized. Typical preparation of these complexes included simple steps: a slurry of ligand (*i.e.* CPE, CPP, CPPP or CPP-2) was prepared in water or in water-ethanol mixture; in this a solution of Mn(CH₃COO)₂·4H₂O was added, and the resulting mixture was irradiated in a microwave oven for 2 to 6 minutes at medium power level (600 W) maintaining the occasional shaking. Proposal structures of complexes are shown by formulae **14-17**. The antibacterial activity of the ligands and complexes was studied. Additionally, the Chinese-lantern-type Co₂(O₂CBut)₄{2,6-(NH₂)₂C₅H₃N}₂ complex reacted with RCN (R = Me or Pr) under microwave irradiation to give the mononuclear amidine complexes Co(O₂CBut)₂{H₂N(C₅H₃N)NHC(R):NH} (R = Me or Pr) (Bokach et al, 2006).

Al-containing mesoporous silicates (Al-MCM-41 and Al-HMS) supported Mn(salen) catalysts were prepared by three different methods: impregnation of salen ligand and support with dichloromethane and then irradiated by microwave (method A), direct solid-state interaction between salen complex and support under microwave irradiation (method B), as well as the conventional ion exchange (method C) (Yin et al, 2005; Zhang et al, 2003). The effect of catalyst preparation methods on the catalytic activity and selectivity in the styrene epoxidation indicate that the catalyst of Mn(Salen)/Al-HMS-IP prepared by method A showed similar activity to the neat complex and the best selectivity for styrene epoxide. In comparison with the traditional adsorption method, the MW-assisted approach was efficient and environmentally friendly, and improved the loadings of Mn(III)-salen complexes on HMS via a strengthening axial coordination of the surface NH_2 groups of HMS toward the Mn(III)-salen complexes (Fu et al, 2007). The effects of several extrinsic physical fields, such as the magnetic field, the ultrasonic wave and the MW, on the rate and yield of chitosan-Fe(II) complexing reaction were investigated (Jiang et al, 2008), showing that ultrasound had the greatest effect on the reaction rate and complexing capacity, followed by the magnetic field and the MW. A mechanism for the enhancement of the complexing reaction by the three physical fields was proposed.

5. Complexes with S- and N,S-containing ligands

According to the available literature, microwave-synthesized complexes of S-containing ligands without other donor heteroatoms are represented by coordination compounds of dithiolene. Thus, dithiolene-transition metal complexes **18** were obtained by a series of steps (Kim et al, 2009) including microwave heating in the first steps of the mixture of benzaldehyde and KCN in EtOH.

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N,S-Complexes are represented by a series of different types of compounds: thiolates, thioimidazoles, thiazoles, thiosemicarbazones, among others. Thus, the solid phase reaction of 1-alkyl-2-[(*o*-thioalkyl)phenylazo]imidazoles (SRaaiNR) and RuCl_3 on silica gel surface upon MW yielded $[\text{Ru}(\text{SRaaiNR})(\text{SaaiNR})](\text{PF}_6)$ (Mondal et al, 2009). BiPh_3 was treated with thiols of varying pKa and functionality (2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptopyrimidine, 2-mercapto-1-methylimidazole and 2-mercaptobenzoic acid) in a 1:3 ratio under a variety of reaction conditions: with toluene or mesitylene under standard reflux conditions and under microwave irradiation, and solvent free with conventional and microwave heating (Andrews et al, 2007). As a result, several reactions yielded the *tris*-substitution product in good yield and high purity; 2-mercaptobenzoic acid gave the complex Bi_2L_3 in all reactions carried out in solvent and PhBiL when solvent free, both complexes containing the doubly deprotonated dianion ($\text{L} = -\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{S}-$). The authors noted that reactions carried out in the microwave reactor generally gave comparable yields to the conventional methods but in significantly shorter times; however, the solvent free microwave reactions of 2-mercaptobenzoxazole and 2-mercaptopyrimidine caused partial decomposition to give microcrystalline Bi_2S_3 . MWH of racemic *cis*- $[\text{Ru}(\text{bpy})_2(\text{Cl})_2]$ (bpy = 2,2'-bipyridine) or racemic *cis*- $[\text{Ru}(\text{phen})_2(\text{Cl})_2]$ (phen = phenanthroline) with either (R)-(+)- or (S)-(-)-Me *p*-tolyl sulfoxide yielded the ruthenium *bis*(diimine) sulfoxide complexes, for example **19** (Pezet et al, 2000). This source of energy improved both yields and reaction rates with a very good diastereoselectivity (73-76%) and represented a significant advance in the asymmetric synthesis of octahedral ruthenium complexes.

A lot of complexes of thiosemicarbazone and its derivatives have been MW-obtained. Thus, molybdenum(VI) complexes $\text{MoO}_2(\text{L})_2$ of the ligands HL {3,4,5-trimethoxybenzaldehydethiosemicarbazone (TBTSCZH), 3,4,5-trimethoxybenzaldehydesemicarbazone (TBSCZH), 3,4,5-trimethoxybenzaldehydebenzothiazoline (TBBZTH) and 3,4,5-trimethoxybenzaldehyde-S-

benzylidithiocarbazate (TBDTCZH)} were MW-fabricated (Maanju et al, 2007) by the reactions between dioxobis(2,4-pentanedionato-O,O')molybdenum(VI) and the ligands TBTSCZH, TBSCZH, TBBZTH and TBDTCZH by MW-assisted and conventional thermal methods. All four ligands and their complexes were screened for their biological activity on several pathogenic fungi and bacteria and the data show good activity of these complexes and ligands. The synthesis of some Mn(II), oxovanadium(V) and dioxomolybdenum(VI) complexes with 5-chloro-1,3-dihydro-3-[2-(phenyl)ethylidene]-2H-indol-2-one thiosemicarbazone (L¹H) and 5-chloro-1,3-dihydro-3-[2-(phenyl)ethylidene]-2H-indol-2-one semicarbazone (L²H) were carried out in unimolar and bimolar ratios in an open vessel under MW using a domestic microwave oven. In the case of the oxovanadium complexes, the metal was found to be in the penta- and hexa-coordinated environments. The ligands and complexes possessed antimicrobial properties. Trigonal bipyramidal and octahedral complexes of Sn(IV) were synthesized by the reaction of dimethyltin(IV) dichloride with 4-nitrobenzanilidethiosemicarbazone (L¹H), 4-chlorobenzanilidethiosemicarbazone (L²H), 4-nitrobenzanilidesemicarbazone (L³H) and 4-chlorobenzanilidesemicarbazone (L⁴H) from dimethyltin(IV) dichloride and monobasic bidentate ligands using MW as the thermal energy source (Singh et al, 2008). The antifungal, antibacterial and antifertility activities were examined and the results were indeed very encouraging. A series of mixed ligand ruthenium(II) containing diimines and thiosemicarbazones with general formula [Ru(N-N)₂(N-S)](PF₆)₂ where N-N = bipyridine or 1,10-phenanthroline and N-S = 9-anthraldehyde thiosemicarbazone and the 4-alkyl substituted (R = Me, Et and phenyl) analogs were synthesized using microwave energy (Beckford et al, 2009; Beckford et al, 2010). The compounds quenched the fluorescence of the complex between ethidium bromide and calf-thymus DNA with the Stern-Volmer quenching consisted in the range 1.18-2.71·10⁴ M⁻¹. Additionally, the Pd(II) and Pt(II) complexes were synthesized using microwave heating by mixing metal salts in 1:2 molar ratios with heterocyclic ketimines, 3-acetyl-2,5-dimethylthiophene thiosemicarbazone (C₉H₁₃N₃OS₂) and 3-acetyl-2,5-dimethylthiophene semicarbazone (C₉H₁₃N₃OS), obtained by reactions of 3-acetyl-2,5-dimethylthiophene with thiosemicarbazide and semicarbazide hydrochloride (Sharma et al, 2010). The authors proposed that the ligands coordinate to the metal atom in a monobasic bidentate manner and square planar environment around the metal atoms. The antiamebic activity of both the ligands and their palladium compounds against the protozoan parasite *Entamoeba histolytica* was tested. Other data on MW-obtaining thiosemicarbazone complexes were discussed in (Chaudhary et al, 2009; Shen et al, 2008).

In case of thiophene derivatives, MW-assisted condensation of salicylaldehyde with 2-amino-3-carboxyethyl-4,5-dimethylthiophene in the absence of solvent was efficiently performed to form a potentially tridentate Schiff base, 2-(N-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene (HSAT), which acted as neutral tridentate with ONO donor sequence towards the lanthanide(III) ions, forming 1:2 metal-ligand complexes of the type [Ln(HSAT)₂Cl₃] where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) (Kumasi et al, 2009). Additionally, it is known that thiophene can react with elemental iron in the form of metal atoms in cryosynthesis conditions or its carbonyls carrying out the desulfurization of the ligand. In reactions with iron carbonyls, the use of MWH evidently led (Singh et al, 1996) to acceleration of reported reactions of thiophene and its tellurium analogue and its derivatives with [Fe₃(CO)₁₂]. The following dechalcogenation reactions take place, forming binuclear complexes **20-21** (reactions 2). Among other organometallic compounds, prepared this way, it is necessary to mention chromium, molybdenum, and tungsten carbonyls (Van Atta et al, 2000).

Cyanobipyridine-derived zinc(II) *bis*(thiolate) complexes [Zn(L)(SAr)] (L = 2-methyl-4-(4-biphenyl)-6-(2-pyridyl)nicotinonitrile and 2-methyl-4-(4-(diphenylamino)phenyl)-6-(2-pyridyl)nicotinonitrile, Ar = Ph, 4-MeOC₆H₄, 2-naphthalenyl) were prepared rapidly and efficiently by a microwave-assisted cross-coupling/complexation sequence and display luminescence that can be modulated using intrinsic functionality and ancillary ligands (Bagley et al, 2010). Organotin complexes of thiol- and thione-containing Schiff bases were MW-prepared and tested for antifungal activity, using Ph₃SnCl, Ph₃SiCl, Ph₂SnCl₂ as metal source and the sodium salts of ligands, 2-HSC₆H₄N:CMech₂(*i*-Pr) (L¹H) and (*i*-PrCH₂C(Me):NNHC(S)NH₂ (L²H), synthesized by condensation of 4-methyl-2-pentanone with 2-aminobenzenethiol and thiosemicarbazide, respectively (Gaur et al, 2005). Pentacoordinated complexes Ph₃SnL¹, Ph₃SiL¹, Ph₂SnCIL¹, Me₂SnCIL¹, Ph₃SnL², Ph₃SiL² and hexacoordinated complexes Ph₂SnL₂¹ and Me₂SnL₂¹ were isolated and tested against a number of microorganisms exhibiting inhibition of growth of *Aspergillus niger*, *Fusarium oxysporum* and *Alternaria alternata*. MWAS and spectroscopic studies of dimethyl-, diphenyl- and triphenyl- Si(IV) chelates derived from the reactions of organochlorosilanes with the sodium salt of a biologically active N-donor ligand [1-(furan-2-yl)ethylidene][4-[(pyridin-2-yl)sulfamoyl]phenyl]amine was reported (Singh et al, 2005). The biological activity of the ligand and its corresponding complexes with regard to antifungal and antibacterial activity against pathogenic fungi and bacteria was revealed; all the compounds also acted as nematocides and insecticides, by reducing the number of nematodes (*Meloidogyne incognita*) and insects (*Trogoderma granarium*).

Antimony complexes with substituted thioimines (**22**) were prepared by reaction of Ph_3Sb and [1-(2-naphthyl)ethylidene]hydrazinecarbodithionic acid phenyl ester, [1-(2-thienyl)ethylidene]hydrazinecarbodithionic acid phenyl methyl ester, [1-(2-pyridine)ethylidene]hydrazinecarbodithionic acid phenyl ester, and [1-(2-furanyl)ethylidene]hydrazinecarbodithionic acid phenyl ester by MWH (Mahajan et al, 2007). Reactions of Ph_3Sb and monobasic bidentate ligands having N⁺S donor set in 1:1 and 1:2 molar ratios proceeded with the cleavage of the antimony carbon bond of Ph_3Sb and yielded monosubstituted derivatives (reactions 3-4).

The reaction product of 2-hydroxy-N-phenylbenzamide with 2-(2-hydroxyphenyl)-2-(phenylamino)benzothiazoline (H_2 -Saly-BTZ), reacted with $PhSbCl_2$, $SbCl_3$, and $BiCl_3$ under varied reaction conditions (microwave, as well as conventional method) leading to corresponding antimony(III) and bismuth(III) compounds (an example is **23**) (Mahajan et al, 2009). The ligand was found to be bifunctional tridentate, as well as monodentate for different starting materials of metal (Sb/Bi). The complexes were more toxic than the corresponding ligand.

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A highly semiconducting 1D coordination polymer architecture was obtained by the reaction of a Cu^{II} salt with 2,2'-dipyridyldisulfide under microwave solvothermal conditions, proceeding with an unusual C-S and S-S bond cleavage of the 2,2'-dipyridyldisulfide ligand to give $\{[Cu^I(L)_8(SH)_8](BF_4)_n\}$ ($SH = 2$ -pyridylthiolate) and $\{[Cu^{II}(2-dps)_2(\mu-S)](BF_4)_2 \cdot 4CH_2Cl_2\}$ ($2-dps = 2,2'$ -dipyridylsulfide) (reaction 5) (Delgado et al, 2008). The unprecedented architecture of the first compound consisted of a 1D polymeric chain formed by the assembling of Cu_9 cluster cages. In a related report of the same research group, an unprecedented microwave $C(sp^2)$ -S and S-S bond activation of 2,2'-dipyridyldisulfide ($2-dpds$) and the formation of an architecture of coordination networks obtained by reaction of $Cu(HCO_2)_2 \cdot xH_2O$ with $2-dpds$ in the same conditions were described (Delgado et al, 2010). Partial oxidation of 2,2'-dipyridyldisulfide to sulfate was found to take place, resulting a Cu(I) dimetallic complex $[Cu_2(\mu-Hpyt)_2(Hpyt)_4](SO_4) \cdot 5EtOH$ ($Hpyt =$ pyridine-2(1H)-thione), a Cu(I,II) polycationic coordination polymer $[Cu(H_2O)_6][Cu_6(\mu-Hpyt)_{12}](SO_4)_4 \cdot 4H_2O$, and a dimetallic Cu(II) complex $[Cu(2-dps)(\mu-SO_4)(H_2O)]_2 \cdot 3H_2O$. The strong red and yellow-orange luminescence was shown for the first two complexes.

6. σ - and π -organometallic compounds

Microwave heating has been applied to obtain a series of metal complexes with classic ligands forming σ - and π -organometallic compounds: carbonyls, cyclopentadienyls, dienes, and arenes, among others. Generally, as well as for the case of the coordination compounds above, main advantages of MW-application are frequently higher yields and almost always considerably shorter reaction times.

6.1 Carbonyls

Among fundamental generalizing publications on MW-fabricated metal carbonyls, we note a review on Group 6 metals, describing, in particular, metal carbonyls synthesis in a conventional MW-oven (Holder, 2005), and a report (Ardon et al, 2004) dedicated to the preparation of a series of mixed Group 6 metal carbonyl complexes with other ligands (*cis*-[Mo(CO)₄(dppe)], [CpMo(CO)₃]₂, [Cp₂Mo₂(CO)₄(μ -RC₂R)], [CpMo(CO)₂]₂, *cis*-[W(CO)₄(pip)₂], [Cr(CO)₅Cl][NEt₄], where dppe = 1,2-*bis*(diphenylphosphino)ethane, pip = piperidine}. Also, mixed carbonyl-arene complexes are known; thus, the microwave-assisted synthesis of (η^6 -arene)tricarbonylchromium complexes from hexacarbonylchromium and arenes gave high yields of (η^6 -arene)chromium tricarbonyl complexes (Lee et al, 2006). In case of noble metals, by using a gas-loading accessory, microwave-assisted synthesis of Ru₃(CO)₁₂, Ru₃(CO)₉(PPh₃)₃, HRu₃(CO)₉(C $\equiv$ CPh) and H₄Ru₄(CO)₁₂ was performed (Leadbeater et al, 2008). Ligand substitution reactions of Ru₃(CO)₁₂ with triphenylphosphine were also studied in real time by means of a digital camera interfaced with the microwave unit. Microwave-assisted ligand substitution reactions of Os₃(CO)₁₂ in a remarkably short period of time led to the labile complex Os₃(CO)₁₁(NCMe) in high yield without the need for a decarbonylation reagent such as trimethylamine oxide (Jung et al, 2009). Additionally, MWH of Os₃(CO)₁₂ in a relatively small amount of acetonitrile was shown to be a useful first step in two-step, one-pot syntheses of the cluster complexes Os₃(CO)₁₁(py) and Os₃(CO)₁₁(PPh₃). Microwave-assisted reactions of 3,3,3-*tris*(3'-substituted pyrazolyl)propanol ligands [(3-Rpz)₃CCH₂CH₂OH, R = H] and [Re(CO)₅Br] yielded [Re(CO)₃]Br and degradation products [(HpzR)₂Re(CO)₃]Br [R = *t*-Bu (7b), Ph] (Kunz et al, 2009). These complexes were also prepared directly from [Re(CO)₅Br] and the corresponding pyrazoles by microwave-assisted synthesis. Beginning with MO₄⁻ (M = ^{99m}Tc, ^{186/188}Re), the carbonyl precursor [M(CO)₃(H₂O)₃]⁺ was synthesized in 3 min in quantitative yield in a microwave reactor (Causey et al, 2008). When di-picolylic ligand (HL = 5-[*bis*(2-pyridinylmethyl)amino]pentanoic acid) was added to the reaction mixture, the chelate complex [M(CO)₃(L)]⁺ was formed in high yield in 2 min using MWH at 150°C. These and further syntheses under MW-heating represented a move away from traditional instant kits toward more versatile platform synthesis and purification technologies that are better suited for producing modern molecular imaging and therapy agents.

6.2 Cyclopentadienyls

As metal-Cp complexes, MW-obtained ferrocene derivatives are the most common. Among relatively old and already classic achievements in this area, we emphasize the following condensation reactions. Thus, according to the conventional techniques, *Claisen-Schmidt*

template reactions of acetylferrocene **24** and ferrocene carboxaldehyde **26** are usually performed under classical homogeneous conditions in ethanol. Using MWH of the reaction system, it became possible (Villemin et al, 1994) to prepare (reactions 6 and 7) ferrocenylenones **25** and **27** without solvent in presence of solid KOH with higher yields in comparison with those reported earlier. It is noted that the reactions may be accelerated efficiently by microwave irradiation.

Condensation of acetylferrocene

Condensation of ferrocene carboxaldehyde

A significant accelerating effect by MWH for the ligand exchange reaction of ferrocenes was observed; this effect was due to the absorption of microwave energy by the adduct between the ferrocene and the Lewis acid (Okada et al, 2009). Six ferrocenyl α,β -unsaturated ketones, FcCOCH:CHAr (Fc = ferrocenyl, Ar = Ph, 4-MeOC₆H₄, 2-furyl, 4-Me₂NC₆H₄, ferrocenyl, 4-O₂NC₆H₄) were prepared by MW-assisted reaction of ArCHO with FcCOMe in the presence of KF-Al₂O₃ as catalyst (Lu et al, 2003). 1,5-dioxo-3-(*p*-methylbenzyloxyphenyl)[5]ferrocenophane (**28**) was MW-prepared (50 W for 30 min with 80°C) in 2-step reaction from 4-hydroxybenzaldehyde in acetone, 4-methylbenzylbromide, CsCO₃, and further addition of diacetylferrocene in 90% yield (Patti et al, 2009).

Additionally, the species MW-synthesized include ferrocene and acetylferrocene, piano stool complexes such as $\text{CpFe}(\text{CO})_2\text{I}$, $\text{CpFe}(\text{PPh}_3)(\text{CO})\text{I}$, and $\text{CpFe}(\text{PPh}_3)(\text{CO})(\text{COMe})$, and bisphosphine iron complexes. The use of microwave-assisted reactions decreased reaction times while maintaining or improving yields as compared to traditional methods (Garringer et al, 2009). Mixed $(\eta^6\text{-arene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}$ complexes are also known (Roberts, 2006; Roberts, 2006).

Group 4 is represented by all three transition metals (Ti, Zr, and Hf). Thus, the reactions of *bis*(cyclopentadienyl)titanium(IV) chloride with Schiff bases (LH_2), derived by condensing 3-(phenyl/2-chlorophenyl/4-nitrophenyl)-4-amino-5-hydrazino-1,2,4-triazoles with salicylaldehyde or 2-hydroxyacetophenone, were studied both by conventional stirring method and also by using microwave heating, isolating $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{L})]$ in both cases (Banerjee et al, 2008). The ligands behaved as dibasic, tetradentate chelating agents and a six-coordinated structure were assigned to these derivatives. The same precursor was applied in reactions with *bis*(thiosemicarbazones) (H_2L), derived by condensing isatin with different N(4)-substituted thiosemicarbazides, were studied both by a conventional stirring method and also using MW technology isolating binuclear $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2(\text{L})]$ compounds (Banerjee et al, 2009). The ligands and complexes possessed inhibiting potential against various fungal, viral and bacterial strains. Similarly, reactions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2$ with benzil *bis*(hydrazones) (LH_2), derived from benzil and aromatic acid hydrazides (benzoic, 2-chlorobenzoic, 4-chlorobenzoic, 2-methylbenzoic or 4-methoxybenzoic) were studied in anhydrous THF in the presence of *n*-butylamine by both conventional methods and by MWH, isolating binuclear complexes of type $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2(\text{L})]$ (Sinha et al, 2008). The stoichiometric reactions of titanocenedichloride or zirconocenedichloride with monofunctional bidentate ligands **29** and **30**, derived from heterocyclic ketones and semicarbazide hydrochloride and 2-hydroxy-*N*-phenyl benzamide, resulted in the formation of unsymmetrical complexes **31** (reactions 8-II) (Poonia et al, 2007; Poonia et al, 2008). A comparison of conventional and microwave route revealed that the second way was 100 times faster.

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A few of other metal cyclopentadienyls have been also reported, for example a very efficient MWAS of $[\text{RuCp}(\eta^6\text{-naphthalene})][\text{PF}_6]$ (Mercier et al, 2009). The synthesis of cyclopentadienyl *bis*-phosphine ruthenium thiolato complexes of the type $[\text{RuCp}(\text{dppm})\text{SR}]$ ($\text{R} = \text{Ph}, \text{CH}_2\text{CH}_2\text{Ph}, \text{CH}_2(2\text{-furyl}), \text{CH}_2\text{CO}_2\text{Et}, \text{CH}_2\text{CH}(\text{NHAc})\text{CO}_2\text{H}$) from $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$ using conventional heating and MW using a focused monomode reactor was described (Kuhnert & Danks, 2002). Sealed tube microwave dielectric heating of diaryl acetylenes with cyclopentadienyl Co dicarbonyl at elevated temperature in *p*-xylene provided access to metallocenes in both the cyclobutadiene ($\text{Ar}_4\text{C}_4\text{CoCp}$, 3-52% yields) and cyclopentadienone ($\text{Ar}_4\text{C}_4(\text{CO})\text{CoCp}$, 14-85% yields) families (Harcourt et al, 2008). In the case of an especially bulky diarylacetylene (1,1'-dinaphthylacetylene), the microwave approach allowed access to a complex that cannot be readily obtained under traditional thermal conditions.

6.3 Arene complexes

Microwave-mediated syntheses of $[(\eta\text{-arene})(\text{CO})_3\text{Mn}](\text{PF}_6)$ complexes (Dabirmanesh et al, 1997), $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-arene})][\text{PF}_6]$ salts from reactions of $\text{Fe}(\text{C}_5\text{H}_5)_2$ with arenes and chloroarenes, as well as $[\text{Fe}(\eta\text{-arene})_2][\text{PF}_6]_2$ salts from reaction of arenes and FeCl_3 (Dabirmanesh et al, 1993) were reported relatively long ago. Reaction times were reduced from several hours by conventional methods to a few minutes using an unmodified domestic microwave oven. Microwave heating was employed to promote arene displacement in reactions of $[(p\text{-cymene})\text{RuCl}_2]_2$ or $[(1,3,5\text{-C}_6\text{H}_3(i\text{-Pr})_3)\text{RuCl}_2]_2$ with neutral chelate ligands L-L' [L-L' : 1,1'-*bis*(diphenylphosphanyl)methane, 1,1'-*bis*(diphenylphosphanyl)ferrocene, (S)-BINAP, (S,S)-DIOP, N,N'-*bis*(2,4,6-trimethylphenyl)-1,2-ethanediylienediamine], (R)-Ph-PHOX, and 3-(phenylsulfanylpropyl)diphenylphosphine giving $[(\text{arene})\text{Ru}(\mu\text{-Cl})_3\text{-RuCl}(\text{L-L'})]$ in good yield (Albrecht et al, 2009). Also, the MWAS of $(\eta^6\text{-arene})\text{tricarboxylchromium}$ complexes from hexacarbonylchromium with arenes gave high yields of products **32** (reaction 12) (Lee et al, 2006).

6.4 Other organometallics

The effect of the microwave irradiation on the reaction of alkynyl alkoxy *carbene complexes* with urea derivatives was studied (Spinella et al, 2003), showing that in these conditions $(\text{CO})_5\text{W}:\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$ reacted with ureas, $(\text{RNH})\text{C}(\text{O})(\text{NHR}')$ (e.g., $\text{R}, \text{R}' = \text{H}, \text{Me}, \text{allyl}, \text{Et}$), with reduced reaction times to give uracil derivatives **33**. It is noteworthy that the use of large amounts of solvents could be drastically reduced or even avoided and, in any case, reaction times were dramatically shortened. The MWAS of two different types of N-heterocyclic carbene-palladium(II) complexes, $(\text{NHC})\text{Pd}(\text{acac})\text{Cl}$ ($\text{NHC} = \text{N-heterocyclic carbene}$; $\text{acac} = \text{acetylacetonate}$) and $(\text{NHC})\text{PdCl}_2(3\text{-chloropyridine})$, led to drastic reduction in reaction times (20 to 88 times faster, depending on the complex) (Winkelmann & Navarro,

2010). The complex $(\text{IPr})\text{Pd}(\text{acac})\text{Cl}$ [$\text{IPr}=1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$] was similarly obtained. Bridged and unbridged N-heterocyclic carbene (NHC) ligands were metalated under MW-conditions with $[\text{Ir}(\text{COD})\text{Cl}]_2$ to give Ir(I) mono- and biscarbene substituted catalysts $[\text{Ir}(\text{COD})\text{NHC}(\text{Cl})]$ and $[\text{Ir}(\text{COD})(\text{NHC})_2][\text{X}]$ ($\text{X} = \text{I}, \text{PF}_6, \text{BF}_4, \text{CF}_3\text{COO}, \text{OTf}$) (Rentsch et al, 2009). Palladium(II) carbene complexes were also reported in (Scarborough et al, 2009).

Diene derivatives are represented by the first example of microwave-promoted solid-state synthesis of Na complex $[\text{Na}(\text{L})(\mu\text{-EP})\cdot\text{H}_2\text{O}]_2$ derived from a heteromacrocylic compound (Tusek-Bozic et al, 2007). This alkali complex, as a diphosphonate-bridged dinuclear species, was prepared from the 15-membered mixed dioxo-diaza macrocycle 5,6,14,15-dibenzo-1,4-dioxo-8,12-diazacyclopentadeca-5,14-diene (L) by reaction with Na Et [4- α -(benzeneazoanilino)-N-benzyl]phosphonate ($\text{NaEP}\cdot 1.5\text{H}_2\text{O}$). MW-heating of *metal-allyl complexes* can result organic products. Thus, nucleophilic attack of 3-hydroxycoumarin on $\eta^3\text{-}\pi\text{-allyl}$ palladium complex, formed from substituted cinnamyl alcohols **34** ($\text{R}^1 = \text{R}^2 = \text{H}$, MeO , $\text{R}^3 = \text{H}$; $\text{R}^1 = \text{OCH}_2\text{Ph}$, $\text{R}^2 = \text{MeO}$, $\text{R}^3 = \text{H}$) and acetyls **34** ($\text{R}^3 = \text{COMe}$) in the presence of palladium acetylacetonate and triphenylphosphine, resulted in normal addition products like 4-(3'-phenylallyl)-3-hydroxycoumarin, except for cinnamyl acetate, which provided an unusual product, 4-(1'-phenylallyl)-3-hydroxycoumarin, by conventional and MWH (Mitra et al, 2003).

Table 1. Main containing ligands' units present in the studied MW-synthesized complexes.

Pyrazol

Tetrazole

Benzimidazole

Imidazole

Pyrazine

Quinoxaline (benzopyrazine)

1,2,4-Triazole

Pyridine

Sulfamoyl radical

1,10-Phenanthroline

2,2'-Bipyridine

4,4'-Bipyridine

Terpyridine

2,4-pentanedione, an example of a β -diketone

1,3,4-Oxadiazoline

Dimethylglyoxime

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Salen

Chitosan

Thiazole

Thiazoline

Dithiolene moiety

Semicarbazone

Thiosemicarbazone

3,4-Dimethylthiophene

Cymene

Cyclopentadienyl anion

7. Microwave-assisted catalysis using metal complexes

Several reports are dedicated to the use of metal (mainly noble metals, such as Rh, Pd, Os, which in free form are used in catalytic processes) complexes in MWAS or rearrangements of organic compounds. Thus, a highly efficient C-C bond cleavage of unstrained aliphatic ketones bearing β -hydrogens with olefins was achieved using a chelation-assisted catalytic system consisting of $(\text{Ph}_3\text{P})_3\text{RhCl}$ and 2-amino-3-picoline by MW under solvent-free conditions (Ahn et al, 2006). The addition of cyclohexylamine catalyst accelerated the reaction rate dramatically under microwave irradiation compared with the classical heating method. Microwave-assisted Rh-diphosphane-complex-catalyzed dual catalysis, providing [2+2+1] cycloadducts by sequential decarbonylation of aldehyde or formate and carbonylation of enynes within a short period of time, was reported (Lee et al, 2008). Various O-, N-, and C-tethered enynes were transformed into the corresponding products in good yields. The first enantioselective version of this microwave-accelerated cascade cyclization was realized. In the presence of chiral Rh-(S)-bisbenzodioxanPhos complex, the cyclopentenone products were achieved with ee values up to 90%. Osmium complex $(\mu\text{-H})\text{Os}_3(\mu\text{-O:CPh})(\text{CO})_{10}$ was an active catalyst for the allylic rearrangement N-allylacetamide under MW-radiation (Afonin et al, 2008).

An efficient method for intermolecular hydroarylation of aryl and aliphatic alkenes with indoles using a combination of $[(\text{PR}_3)\text{AuCl}]/\text{AgOTf}$ as catalyst under thermal and microwave-assisted conditions was developed (Wang et al, 2008), achieving the gold(I)-catalyzed reactions of indoles with aryl alkenes in toluene at 85°C over a reaction time of 1-3 h with 2 mol% of $[(\text{PR}_3)\text{AuCl}]/\text{AgOTf}$ as catalyst (yields 60-95%). Under microwave irradiation, coupling of unactivated aliphatic alkenes with indoles gave the corresponding adducts in up to 90% yield. Additionally, metal acetates were found to be effective catalysts; thus, a rapid and efficient method for the synthesis of β -aryllalkenyl nitriles by a one-pot three component coupling reaction of diphenylacetylene, $\text{K}_4\text{Fe}(\text{CN})_6$, and aryl halides using $\text{Pd}(\text{OAc})_2$ as a catalyst and water as a solvent under MW (Velmathi et al, 2010). The method employed a cyanide source which is safe and inexpensive. Copper-catalyzed cyanation of aryl halides was improved to be more economical and environmentally friendly by using water as the solvent and ligand-free $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ as the catalyst under MW (Ren et al, 2009). The suggested methodology was applicable to a wide range of substrates including aryl iodides and activated aryl bromides.

8. Conclusions

In the coordination and organometallic chemistry, the microwave-assisted synthesis is not developed sufficiently as for the preparation of inorganic compounds, composites and materials or in the organic synthesis, where microwave heating can be considered as a common preparative tool. However, during the last decade a considerable growth of related reports has been registered. The most number of reports corresponds to MW-reactions of the N-, N,O-, and N,S-containing ligands with sources of metal ions. Some MW-fabricated classic π - and σ -organometallic compounds are also presented.

Practically in all reports, main attention of researchers is paid to extreme fastness of MW-assisted reactions in comparison with classic protocols. The same reactions in the MW-field take place in 10-100 times more rapidly. Moreover, higher or comparable yields are frequently reported. Sometimes, the MW-route leads to products, which it is impossible to get *via* traditional routes, for instance preparation of several metal cluster complexes.

Despite of the development of novel synthesis techniques in chemistry and especially nanotechnology (for example, laser-, sputtering-, CVD-, electron- and ion-beam-, radiation-, or combustion-assisted methods, among many others, the microwave heating remains very attractive for chemists due to its obvious advantages, noted at the beginning of this chapter.

9. Abbreviations

2-dpds = 2,2'-dipyridyldisulfide

acac = acetylacetonate

APBMPA = (3-aminopropyl)*bis*(2-pyridylmethyl)amine

BMPA = *bis*(2-pyridylmethyl)amine

bbi = 1,1'-(1,4-butanediyl)*bis*(imidazole)

bpd = 3-bromo-2,4-pentanedionate ion

bpy, bipy = 2,2'-bipyridine

bpydc = 2,2'-bipyridine-5,5'-dicarboxylate

BTEC = 1,2,4,5-benzenetetracarboxylate anion

CDEPE = N,N'-*bis*(3-carboxy-1-oxopropyl)-1,2-diethylethylenediamine

CDEPE-2 = N,N'-*bis*(3-carboxy-1-oxoprop-2-enyl)-1,2-diethylethylenediamine
 CDMPE = N,N'-*bis*(3-carboxy-1-oxoprop-2-enyl)-1,2-dimethylethylenediamine
 CDMPE-2 = *bis*(3-carboxy-1-oxoprop-2-enyl)-1,2-dimethylethylenediamine
 CPE = N, N'-*bis*-(3-carboxy-1-oxoprop-2-enyl)-1,2-ethylenediamine
 CPP = N,N'-*bis*-(3-carboxy-1-oxo-prop-2-enyl)-1,2-phenylenediamine
 CPP-2 = N,N'-*bis*-(3-carboxy-1-oxoprop-2-enyl)-1,2-phenylenediamine
 CPPP = N,N'-*bis*-(2-carboxy-1-oxophenelenyl)-1,2-phenylenediamine
 DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene
 dcmb = 4,4'-dimethoxycarbonyl-2,2'-bipyridine
 DMAD = di-methylacetylenedicarboxylate
 DMAE = dimethylaminoethanol
 DMF = N,N-dimethylformamide
 dppe = 1,2-*bis*(diphenylphosphino)ethane
 2-dps = 2,2'-dipyridylsulfide
 EMim = 1-ethyl-3-methylimidazolium
 H₂bzimp = 2,6-*bis*(benzimidazol-2-yl)pyridine
 Hdpa = *bis*(2-pyridyl)amine
 H₂NDC = 2,6-naphthalenedicarboxylic acid
 H₂oba = 4,4'-oxydibenzoic acid
 H₂-Saly-BTZ = 2-(2-hydroxyphenyl)-2-(phenylamino)benzothiazoline
 HSAT = 2-(N-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene
 H₂TPyP = 5,10,15,20-*tetrakis*(2-pyridyl)porphyrin
 H₃IDC = 4,5-imidazoledicarboxylic acid
 Hpyt = pyridine-2(1H)-thione
 H₃TMA = trimesic acid
 H₄btec = 1,2,4,5-benzenetetracarboxylic acid
 LiPBMPA = 3-[*bis*(2-pyridylmethyl)amino]propanoate
 MW = microwave irradiation
 MWAS = microwave-assisted synthesis
 MWH = microwave heating
 Mg(TBPor) = 5,10,15,20-*tetrakis*(4-tert-butylphenyl)magnesium porphyrins
 mimp = 2-methyliminomethylphenolate anion
 MORE = microwave-induced organic reaction enhancement
 MPBMPA = Me 3-[*bis*(2-pyridylmethyl)amino]propanoate
 MWAACVD = microwave plasma aerosol-assisted chemical vapor deposition
 MWPECVD = microwave plasma enhanced chemical vapor deposition
 OA = oleic acid
 OAm = oleylamine
 PABMPA = 3-[*bis*(2-pyridylmethyl)amino]propanamide
 PDHEP = [N,N'-*bis*(1,5-dimethylhexyl)-3,4:9,10-perylenebis(dicarboximide)]
 phen = 1,10-phenanthroline
 pip = piperidine
 PNBMPA = 3-[*bis*(2-pyridylmethyl)amino]propionitrile
 pytrz = 2-(1-alkyl/aryl-1H-1,2,3-triazol-4-yl)pyridine
 pyz = pyrazolyl ligand
 Pz = pyrazine

PzAM = pyrazine carboxamide

PzCA = pyrazine carboxylic acid

saoH₂ = salicylaldehyde

SRaaiNR = 1-alkyl-2-((o-thioalkyl)phenylazo)imidazoles

tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine

TBHP = *tert*-butyl hydroperoxide

TBBZTH = 3,4,5-trimethoxybenzaldehydebenzothiazoline

TBDTCZH = 3,4,5-trimethoxybenzaldehyde-S-benzylthiocarbamate

TBSCZH = 3,4,5-trimethoxybenzaldehydesemicarbazone

TBTSCZH = 3,4,5-trimethoxybenzaldehydethiosemicarbazone

tipsepd = 3-((triisopropylsilyl)ethynyl)-2,4-pentanedionate ion

TRISPHAT-N = 2,3-pyridinyldioxy anionic phosphate

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The book offers comprehensive coverage of the broad range of scientific knowledge in the fields of advances in induction and microwave heating of mineral and organic materials. Beginning with industry application in many areas of practical application to mineral materials and ending with raw materials of agriculture origin the authors, specialists in different scientific area, present their results in the two sections: Section 1-Induction and Microwave Heating of Mineral Materials, and Section 2-Microwave Heating of Organic Materials.

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