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Preliminary communication

Application of microwave dielectric loss heating effects for the rapid and convenient synthesis of organometallic compounds

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Abstract

Di-olefin-rhodium(I) and -iridium(I) complexes have been synthesised in a sealed Teflon container by use of microwave heating. The products are obtained in excellent yields and in less than 1 minute compared with many hours by conventional reflux techniques. Furthermore, the sandwich cation $[\text{Rh}(\eta\text{-C}_5\text{H}_5)_2]^+$ can be obtained directly from $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ and C_5H_6 by this new technique.

The applications of microwaves for accelerating organic reactions [1,2], the dissolution of geological samples by mineral acids [3], and solid state reactions [4] is well documented [5]. For solution reactions the most effective results have been obtained by use of sealed Teflon containers which can sustain temperatures of 250 °C and pressures of 80 atm [6]. In this communication we describe for the first time the application of these techniques to the synthesis of organometallic compounds.

The rhodium(I) and iridium(I) dimers $[\text{M}_2\text{Cl}_2(\text{di-olefin})_2]$ (**1**) (M = Rh, Ir) which are widely used starting materials are conventionally synthesised from $\text{MCl}_3 \cdot x\text{H}_2\text{O}$ and the olefin in aqueous alcohol. Good yields are obtained only after many hours (4–36) of refluxing [7–9]. Using a sealed Teflon container [6] and a microwave oven operating at a frequency of 2450 MHz with a power of 500 Watts we found that these dimers **1** can be conveniently synthesised from the same reagents in good yields and in less than 1 minute. In the reactions 0.2–1.0 g of the platinum metal salts were used with a reaction volume of 15 cm³.

The range of compounds synthesised in this manner, their yields and the reaction mixtures and times are summarised in Table 1. The accelerations are very large, and are comparable with those described previously for organic reactions [1,2]. Interestingly, with freshly distilled cyclopentadiene the product is the sandwich cation $[\text{Rh}(\eta\text{-C}_5\text{H}_5)_2]^+$ (**2**) rather than the chloro-bridged dimer. By conventional techniques the synthesis of **2** has only been achieved previously by using the Grignard reagent $\text{C}_5\text{H}_5\text{MgBr}$ [10]. This result emphasises the fact that the microwave tech-

Table 1

[M₂Cl₂(di-olefin)₂] complexes formed using microwave heating

Product ^a	Reaction mixture	Reaction time (seconds)	Yield (%)
[Rh(C ₈ H ₁₂)Cl] ₂	13 cm ³ EtOH/H ₂ O (5/1) 2 cm ³ C ₈ H ₁₂	50	91
[Rh(C ₇ H ₈)Cl] ₂	13 cm ³ EtOH/H ₂ O (5/1) 2 cm ³ norbornadiene	35	68
[Ir(C ₈ H ₁₂)Cl] ₂	13 cm ³ EtOH/H ₂ O (5/1) 2 cm ³ C ₈ H ₁₂	45	72
[Rh(η-C ₅ H ₅) ₂]PF ₆ ^b	14 cm ³ MeOH 1 cm ³ C ₅ H ₆	30	62

^a All products were characterised by chemical and spectroscopic analysis. ^b Methanolic NH₄PF₆ added to the reaction product to obtain the yellow salt.

nique not only provides a means of speeding up known reactions, but can also result in new chemistry.

With some olefins, e.g. cyclooctene and cyclooctatetraene, the complexes were not isolated and rhodium metal was the major product. Presumably in these cases either the rate of reduction is faster than that of complex formation, or the olefin complex formed is not stable under the reaction conditions. We conclude that the latter is more likely since it was found that reactions which gave products stable to decomposition above 160 °C gave no metal provided the reaction times were kept to less than one minute.

The same procedures have been used to synthesise [Ru(η-C₆H₆)Cl₂]₂ from RuCl₃ · xH₂O and 1,3-cyclohexadiene in aqueous ethanol [11]. A reaction time of 35 sec gave a yield of 89%.

These very large accelerations of reaction rates should not be attributed to specific molecular absorption effects, but rather to macroscopic dielectric loss heating effects associated with the solvents. Both water and alcohols have high dielectric loss tangents and are effective in converting microwave energy into thermal energy [12]. These efficient heating effects very rapidly lead to a "pressure cooker effect" in the sealed Teflon container due to the volatility of the solvents. In the case of these specific reactions the formation of HCl during the reaction serves to increase the pressure build-up within the Teflon reactor. Indeed, when the reactions were allowed to proceed for more than one minute the pressure release valve incorporated into the Teflon container came into operation, indicating that 80 atm pressure had been exceeded.

The rapid heating observed in these reactions could also be enhanced by Maxwell–Wagner interfacial dielectric loss mechanisms [12]. These are known to occur when small amounts of a conducting phase are in contact with a non-conducting medium, e.g. when wax and water are exposed to microwaves and radiofrequencies [12]. In these reactions the alcohol/water-olefin mixture is not miscible and the build up of charge at the interfaces could provide the necessary conditions for operation of the Maxwell–Wagner mechanism.

Caution. The microwave reactions described in this paper should not be repeated in closed vessels without a pressure release device since this could result in violent explosions.

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