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Preliminary Communication

The synthesis of iron sandwich complexes by microwave dielectric heating using a simple solid CO_2-cooled apparatus in an unmodified commercial microwave oven

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Abstract

Improved syntheses of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})][PF_6]$ salts are reported using a simple apparatus in an unmodified commercial microwave oven. The syntheses of $[Fe(\eta\text{-arene})_2][PF_6]_2$ salts are also reported.

Microwave dielectric heating effects are being used increasingly in both organic and organometallic synthesis. Many reactions can now be conducted in conventional, commercially available microwave ovens. A recent review [1] highlights this growth in interest and also gives details of modifications for more sophisticated experiments. One of the attendant problems in the use of microwave ovens for synthesis is the difficulty of containing volatile liquids which has necessitated the introduction of an external cooling system via copper ports. Alternatively, reactions can be carried out in microwave bombs, but some recent experiences [2] have shown this to be rather unpredictable. We have developed a very simple technique which solves some of these problems. This makes use of the lack of a dipole moment in carbon dioxide which renders solid CO_2 transparent to microwaves. We have, for example, observed little or no sublimation of solid CO_2 after 4 min in a microwave oven at the highest setting. As a result of this, we have devised an extremely simple apparatus consisting of a 250 ml beaker (as the reaction vessel) and a 150 ml beaker with a 2 cm flanged lip placed as a cover over the larger beaker to act as a "cold finger". We have conducted over 100 reactions on a 2–4 gram scale using this apparatus, with no problems of solvent escape even when using volatile solvents such as benzene.

As part of our work on synthesis of iron sandwich complexes, we decided to evaluate the potential of microwave technology as a synthetic tool in this area. We found that the synthesis of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]$ salts [3,4] (eqn. (1)) was greatly facilitated by the use of microwave radiation, reaction times being cut from 4–6 h to less than 4 min with significantly improved yields (Table 1). Results of experiments aimed at optimisation of yields are given in Table 2 for the important chlorobenzene complex. From these results it is clear that only a 2–3 fold excess of the arene is needed, which is important if the arene used is expensive. The optimum yield obtained of 56% is again a significant improvement on those from conventional methods. In contrast to the $[Fe(\eta\text{-arene})_2]$ complexes (see below), no inter- or intra-molecular rearrangement of the methylated arenes occurs in the reaction.

$$\text{arene} + Fe(C_5H_5)_2 \xrightarrow[\text{(ii) } HPF_6]{\text{(i) } AlCl_3/Al} [Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]PF_6 \qquad (1)$$

Table 3 lists the results for the synthesis of the $[Fe(\eta\text{-arene})_2]$ complexes [13] (eqn. (2)).

$$\text{arene} + FeCl_3 \xrightarrow[\text{(ii) } HPF_6]{\text{(i) } AlCl_3} [Fe(\eta\text{-arene})_2][PF_6]_2 \qquad (2)$$

TABLE 1. Yields of $Fe[(\eta\text{-}C_5H_5)(\eta\text{-arene})]$ hexafluorophosphate [a] from microwave experiments

Arene	Yield (%) [b]	
Benzene	88	(30–50 [c,d])
Toluene	53	(40 [e])
o-Xylene	81	(40 [e])
m-Xylene	48	(40 [c])
p-Xylene	62	(45 [e])
Mesitylene	80	(42 [e])
Durene	87 [c,f]	(30–50 [c])
Pentamethylbenzene	99	(30–50 [c])
Hexamethylbenzene	58 [c,f]	(30–50 [c,d])

[a] Ratios of reactants: Arene:ferrocene:$AlCl_3$:Al = 1:1:2:1; reaction time 3 min on medium setting. [b] Yields using conventional methods in parentheses. [c] Ref [6]. [d] Isolated as tetrafluoroborate. [e] Ref [7]. [f] Reaction time 4 min.

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TABLE 2. Yields of [Fe(η-C_5H_5)(η-chloroarene)] hexafluorophosphates from microwave experiments [a]

Chloroarene	[Chloroarene] (M)	Reaction time (min)	Yield [b] (%)
Chlorobenzene	0.01	1.0	25 (25 [c])
Chlorobenzene	0.02	1.6	42
Chlorobenzene	0.03	2.0	56
Chlorobenzene	0.03	2.5	48
Chlorobenzene	0.04	2.5	34
Chlorobenzene	0.04	3.0	34
2-chloro-*p*-xylene	0.01	1.0	84
1,2-dichlorobenzene	0.02	4.0	42 (40–60 [c])

[a] Microwave setting, MEDIUM. Ferrocene (0.01 mol), $AlCl_3$ (0.02 mol), Al (0.01 mol). [b] Yields from conventional methods in parentheses. [c] Ref. [8]. Isolated as tetrafluoroborate.

TABLE 3. Yields of [Fe(η-arene)$_2$] hexafluorophosphates from microwave experiments [a]

Arene	Yield [b] (%)	
Benzene	2	(52 [c], 76 [d])
Toluene	9	(65 [d])
o-Xylene	27	(69 [e])
m-Xylene	25	(76 [e])
p-Xylene	20	(51 [c], 72 [e])
Mesitylene	21	(86 [d], 78 [f])
Durene	21	(75 [f])
Pentamethylbenzene	37	(82 [f])
Hexamethylbenzene	28	(88 [f])
2-chloro-*p*-xylene	– [g]	

[a] Ratio of reactants: arene:$AlCl_3$:$FeCl_3$ = 2:2:1; reaction time 2 min on high setting. [b] Total yields of complexes formed. Yields from conventional methods in parentheses. [c] Ref. [9]. [d] Ref. [10]. [e] Ref. [11]. [f] Ref. [12]. [g] The arene was completely dechlorinated during reaction yielding a complex mixture of methylated benzene complexes.

In this instance, yields were generally much lower * than those obtained by conventional means. There was also considerable rearrangement of the original arene by both inter- and intra-molecular migration of the methyl groups. Thus pentamethylbenzene gave a mixture of bis-iron complexes containing 7% of durene, 54% of pentamethylbenzene, and 39% of hexamethylbenzene complexes **. Control experiments involving use of arene and $AlCl_3$ mixtures alone gave the same product ratios, indicating that, in contrast to the [Fe(η-C_5H_5)(η-arene)] syntheses, rearrangement occurs prior to complexation.

A typical procedure is as follows. Ferrocene (0.01 mol), Al powder (0.01 mol) and $AlCl_3$ (0.02 mol) were ground together in a mortar. The arene was added and the mixture reground. The intimate mixture then rapidly transferred to the microwave apparatus (Sharp Easy Chef R5A53, 850 watt) and heated for the appropriate time with a beaker of water (60 ml) placed alongside the reaction vessel to absorb excess microwave radiation. (Reaction times longer than 4 min resulted in considerable charring). The complexes were isolated by the conventional work-up of adding water and precipitating with HPF_6 from the aqueous solution. Products were characterised by ^1H and ^{13}C NMR spectroscopy and compared with published data [5].

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* This may be due to the absence of powdered metal which is known to couple effectively with microwave fields [14].

** The composition of the mixture of bis arene iron complexes was determined by decomposition with aqueous methylamine followed by extraction with CS_2 and analysis by GLC.