

Synthesis and decomplexation of (η -arene)(η -cyclopentadienyl)-iron(II) hexafluorophosphates using microwave dielectric heating

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A detailed study of the synthesis of (η -arene)(η -cyclopentadienyl)iron(II) hexafluorophosphates has been made using microwave dielectric heating. Reactions were carried out in a conventional 850 W microwave oven in a very simple solid CO₂-cooled apparatus. A wide range of arene ligands were used. The microwave technique reduced the normal reaction times for the AlCl₃-mediated ligand exchange with ferrocene (with aluminium powder to prevent ferricinium ion formation) from several hours to a few minutes and generally resulted in higher yields. 1,2,4-Trichlorobenzene was found to be an excellent solvent for such reactions. A preliminary survey of the efficacy of the type of the metal powder used revealed that zinc and copper were as effective as aluminium, but that nickel and tin gave little or no reaction. Better yields were usually obtained when an excess of ferrocene was used. This was particularly true of alkylarene ligands where almost quantitative yields were obtained in some cases. The microwave method is particularly suited to the synthesis of bis and more highly complexed species. Arylamine complexes can also be made in high yields. Complexes of triphenylphosphine are reported together with a wide range of other arenes.

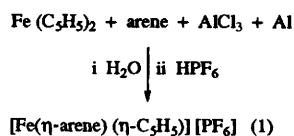
Decomplexation of these complexes can be efficiently achieved by a slight variant of the above microwave procedure. High yields of free ligand were obtained by irradiating an admixture of the complexes with flaked graphite.

Introduction

We recently reported the microwave-assisted syntheses of (η -arene)(η -cyclopentadienyl)iron(II) hexafluorophosphates [FeAr(cp)][PF₆] using a simple solid CO₂-cooled apparatus in a conventional domestic microwave oven.¹ The key to the success of the method is the use of solid CO₂ as coolant. Carbon dioxide has no dipole moment and is thus transparent to microwave radiation. This makes reaction vessel design very easy and obviates the need for expensive modifications of domestic ovens. The reactions proceeded rapidly with generally improved yields over conventional methods.² We have now modified and extended the range and scale of these syntheses and have also developed a very simple method of decomplexation. We now provide a detailed report of these synthetically useful reactions.

Results and discussion

In our previous work on microwave-assisted syntheses of [FeAr(cp)] salts by ligand exchange [eqn. (1)], no solvent was used and reactions were conducted by irradiation of an intimately ground mixture of reagents.



It seemed to us beneficial to have as many of the reagents in solution as possible. Accordingly, we examined a range of solvents which led to the identification of 1,2,4-trichlorobenzene (TCB) as the solvent of choice. (Many of the more polar solvents, such as DMSO, gave charred products and/or ferricinium salts.) TCB has a number of advantages for use in microwave syntheses. It is cheap, has a high boiling point (214 °C) and possesses a small but significant dipole moment³

which makes it an absorber of microwave radiation. Additionally, the high chlorine content reduces any fire risk.⁴ Unlike the mono- and di-chlorinated benzenes, trichlorobenzenes do not form [FeAr(cp)] complexes owing to the increased electron withdrawal by the extra chlorine substituent.

Before exploring the range of microwave-assisted [FeAr(cp)][PF₆] syntheses, we firstly examined the efficacy of metals other than the commonly employed aluminium. The results appear in Table 1. Zinc and copper were equally as effective as aluminium but nickel and tin gave no product. Quantitative comparisons are not possible since the particle size of the powder will have a significant effect on yields. However, we have not observed any marked differences between 74 and 20 micron aluminium powders when used in these reactions. The ratio of metal to other reagents is important. A 2–4 fold excess of aluminium has been used throughout which seems to give the best yields overall. The ease and rapidity of the microwave-assisted [FeAr(cp)][PF₆] synthesis enabled us to study a very wide range of arenes over a relatively short period of time. The results are presented in Tables 2–5. No attempt has been made to optimise yields, our purpose being to determine the range of arene sandwich complexes which are amenable to microwave synthesis. For example, the AlCl₃ used was not resublimed prior to use whereas purified AlCl₃ usually gives enhanced yields.⁵ Generally, the use of TCB as a solvent improved the yields of complexes of solid arenes but sometimes reduces yields for liquid arenes.

(i) Halogenoarene complexes

The effect of solvent is seen for the synthesis of halogenoarene complexes in Table 2. Thus, the yields of the important chlorobenzene complex obtained without TCB were substantially higher than those with solvent (Expts. 4 and 2, respectively). It became clear, however, that improved yields can be obtained using an excess of ferrocene over the arene. Thus, a 65% yield of the chlorobenzene complex was obtained

Table 1 Yields^a of [Fe(η -C₆H₅Cl)(η -C₅H₅)]PF₆ using various finely divided metals

	Metal	Fe	Zn	Sn	Cu	Cu(bronze)	Ni	Al
	% yield	11	26	0	32	14	0	29, 52 ^b , 20 ^c , 21 ^d

^a Standard conditions: PhCl (0.03 mol), ferrocene (0.01 mol), AlCl₃ (0.02 mol), metal powder (0.02 mol). Microwave setting, medium. Reaction time 2 min, no solvent. ^b 0.01 mol Al. ^c 0.04 mol Al. ^d 0.10 mol Al.

Table 2 Yields^a and reaction conditions for the synthesis of [Fe(η -halogenoarene)(η -cp)] hexafluorophosphates using microwave dielectric heating^b

Expt. no.	Halogenoarene	Time (min)	Reagent ratios				Scale ^c	Yield (%)
			Halogenoarene	Ferrocene	AlCl ₃	Al		
1	PhCl	4	1	3	6.1	7.9	0.01	65 (42) ^d
2	PhCl	3	3.1	1	2	1	0.1	19
3	PhCl	7	1	2	4	5.2	0.05	48
4	PhCl ^e	2	3	1	2	1	0.01	56
5	PhCl ^f	3	4	1	4	8	0.01	46
6	1,2-Cl ₂ C ₆ H ₄	4	2	1	2	1	0.01	42 (40 ^e , 62 ^g)
7	1,2-Cl ₂ C ₆ H ₄	5	2	1	3	2	0.1	47
8	1,3-Cl ₂ C ₆ H ₄	2	2	1	2	1	0.01	22 (40–60) ^g
9	1,4-Cl ₂ C ₆ H ₄	2	2	1	2	1	0.01	22 (6) ^g
10	PhF	4	1	1	2	2	0.08	47 (10) ^g
11	PhF	3	2.1	1	2	1.5	0.1	25
12	PhF	8	1	2	4	6	0.1	38 ^h
13	1,2-F ₂ C ₆ H ₄	8	1	2	4	6	0.05	14 (26) ⁱ
14	1,4-F ₂ C ₆ H ₄	3	1	1	2	4	0.02	7
15	1,2-F,ClC ₆ H ₄	8	1	2	4	6	0.05	24
16	1,2-F,ClC ₆ H ₄	4	2	1	2	3	0.05	14
17	1,2-F,MeC ₆ H ₄	3	2	1	2	1.1	0.05	94
18	1,3-F,MeC ₆ H ₄	3	2	1	2	2	0.02	31
19	1,4-F,MeC ₆ H ₄	4	2	1	2	2.5	0.04	29 (22) ^g
20	PhBr	4	1	1	2	2	0.05	32 (–) ^j

^a Yields using conventional method appear in parentheses. ^b Microwave setting medium. Volume of solvent was varied according to the reaction scale (e.g. 0.01 mol, 10 cm³; 0.1 mol, 30 cm³). ^c Mol of reagent in excess. ^d S. I. S. Fernando and R. M. G. Roberts, unpublished result. ^e No solvent used. ^f 1,1'-Dimethylferrocene used instead of ferrocene. ^g Values quoted in ref. 6. ^h Contaminated with 10% chlorobenzene. ⁱ K. Bambridge and R. M. G. Roberts, unpublished result. ^j No yields quoted, ref. 7.

using a ferrocene: arene ratio of 3:1 (Expt. 1). Where an excess of ferrocene is used, the ratio of ferrocene: AlCl₃: Al of 1:2: ~3 is maintained.

One important feature of the work described in Table 2 (and subsequent work) is that reactions can be conducted on a 20 g scale with the appropriate adjustment of reaction times (Expts. 2, 7, 11). Care should be exercised, however, since too prolonged an irradiation causes yields to drop due to thermal decomposition. Other reactions can also occur as in the synthesis of the fluorobenzene complex where a significant amount of halogen exchange occurred on prolonged reaction (Expt. 12).

The yields of the halogenobenzene complexes were generally rather better than those using the conventional method of synthesis.² Of particular note is the successful synthesis of the bromobenzene complex in reasonable yields (Expt. 20). Hitherto, this complex has proved rather elusive,^{7,8} since ligand exchange of ferrocene with bromobenzene is usually accompanied by significant debromination.

(ii) Arene and alkylarene complexes

Details of the synthesis of arene and alkylarene complexes appear in Table 3. Again, better yields were obtained using the microwave method compared with conventional procedures. In particular, considerable improvements in yield were found when an excess of ferrocene was used. For both diphenylmethane and triphenylmethane, the stoichiometry of the complexes can be varied simply by altering the arene to ferrocene ratio (Expts. 24–27). In the case of the triphenylmethane bis complex, it is noted that carbons 2 and 6 of the complexed phenyl group are diastereotopic and thus give separate signals in the ¹³C

NMR spectrum at 87.20 and 87.00 ppm. An excess of ferrocene again resulted in substantially higher yields in both cases. Similar results were obtained for the terphenyl series. A 1:1 ratio of *m*-terphenyl (1,1':3,1''-terphenyl) to ferrocene gave a total yield of only 7% (62% mono, 38% bis as determined from the ¹H NMR spectra, Expt. 33), whereas a five-fold excess of ferrocene gave a 64% yield (32% mono, 68% bis). An even bigger improvement was seen in the case of *p*-terphenyl (1,1':4,1''-terphenyl) (Expts. 35–37). An interesting feature of these results is the occurrence of appreciable amounts of the bis complex even when a large excess of arene is used (Expts. 34, 37). This is a rather surprising result since inductive effects appear to be transmitted from one outer ring to the other in terphenyls¹⁴ and the Fe(cp)⁺ moiety is electron withdrawing. This apparent activation to further complexation by Fe(cp)⁺ is not readily explained.

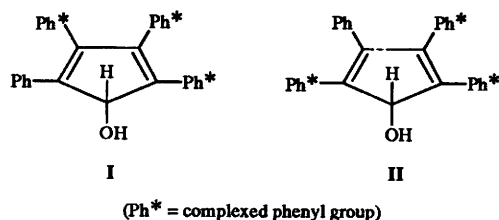
Reduction accompanies complexation for some arenes, particularly for polycyclics such as anthracene (Expt. 40). In the latter case, omission of aluminium metal resulted in a small yield of the dihydroanthracene complex. However, no product was formed when the metal was present suggesting that reduction is effected by other species present. Sutherland¹⁵ has made a detailed study of the hydrogenation accompanying the synthesis of naphthalene complexes and has concluded that a radical process occurred mediated by AlCl₃. The latter is thought to abstract a hydride ion from the solvent, decalin, followed by homolytic fission of the Al–H bond. Under our conditions, no hydrogenation of the naphthalene complex occurred (Expt. 38) presumably because the solvent TCB is a very weak hydride donor. The very low yield observed for the

Table 3 Yields^a and reaction conditions for the synthesis of arene and alkyl arene complexes [FeAr(cp)] [PF₆]^b using microwave dielectric heating^b

Expt. no.	Arene	Time (min)	Reagent ratios				Scale ^c	Yield (%)
			Arene	Ferrocene	AlCl ₃	Al		
21	PhH	3.5	3.6	1	2	1	0.05	23 (30–50) ^d
22	PhMe	3	4.3	1	2	1.2	0.03	54 (40) ^d
23	1,2,4,5-Me ₄ C ₆ H ₂	3	2	1	2	1.2	0.01	36 (30–50) ^d
24	Ph ₂ CH ₂	4	4	1	2	1.1	0.05	55 ^e (26) ^f
25	Ph ₂ CH ₂	4	1	5	10	10	0.01	79 ^g
26	Ph ₃ CH	3	1	2	4.5	3.6	0.03	61 ^e (26) ^h
27	Ph ₃ CH	4	1	5	10	10	0.01	94 ^g
28	(<i>E</i>)PhCH=CHPh	3	1	2	4	3.7	0.01	57 ^e
29	(<i>E</i>)PhCH=CHPh	4	1	5	10	10	0.01	58 ^g
30	Ph ₂	3	1	2.6	5.4	2.6	0.01	70 ^e (40) ⁱ
31	Ph ₂	4	1	5	10	10	0.01	94 ^j
32	1,1':3,1''-Terphenyl	4	1	5	10	10	0.01	64 ^g (30–50) ⁱ
33	1,1':3,1''-Terphenyl	4	1	1	2	2	0.1	7 ^k
34	1,1':3,1''-Terphenyl	4	5	1	2	2	0.1	8 ^l
35	1,1':4,1''-Terphenyl	4	1	5	10	10	0.01	99 ^m
36	1,1':4,1''-Terphenyl	4	2	1	2	2	0.02	16 ⁿ
37	1,1':4,1''-Terphenyl	4	5	1	2	2	0.002	15 ^o
38	Naphthalene	2	1	1	2	4	0.01	55 (30) ^p
39	Fluorene	3	1	2	4	3.7	0.01	53 ^e (34) ^d
40	Anthracene	4	1	1	2	0	0.02	5 ^q
41	Anthracene	4	1	1	2	2	0.02	0
42	Phenanthrene	3	1	1	2	2	0.02	40 ^e (10) ^r
43	Acenaphthene	3	1	1	2	4	0.02	40 (14.5) ^d
44	Acenaphthylene	3	1	1	2	4	0.02	12 ^s
45	Tetracyclone	4	1	5.5	12.9	22.4	0.005	42% ^t
46	Tetracyclone	6	1	10.8	24	24	0.005	62% ^u
47	Tetracyclone	3	1	1	3	7.5	0.005	0
48	Decacyclone	3 ^v	1	4	4	8	0.01	5

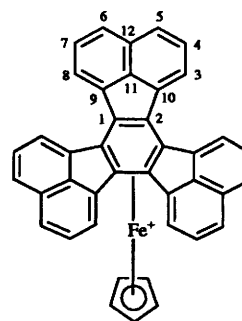
^{a,b,c} As for Table 2. ^d Values in ref. 6. ^e Mono complex. ^f Ref. 9. ^g Bis complex. ^h Ref. 10. ⁱ Ref. 11. ^j 32% Mono, 68% bis complex. ^k 71% Mono, 29% bis complex. ^l 62% Mono, 38% bis complex. ^m 22% Mono, 78% bis complex. ⁿ 88% Mono, 12% bis complex. ^o 80% Mono, 20% bis complex. ^p Ref. 12. ^q Dihydroanthracene complex. ^r Ref. 13. ^s Acenaphthene complex. ^t Largely bis complex. ^u Largely tris complex. ^v Microwave setting high.

dihydroanthracene complex seems to confirm this (Expts. 40, 41). Arene hydrogenation was also found for acenaphthalene (Expt. 44), but no hydrogenation of the exocyclic double bond in stilbene was observed (Expts. 28, 29). Reduction of other functional groups also occurs. With an excess of ferrocene, tetracyclone (tetraphenylcyclopentadienone) undergoes multiple complexation accompanied by reduction of the carbonyl function to the alcohol. Evidence for this comes from the absence of any carbonyl signal at ~ 200 ppm¹⁶ in the ¹³C NMR spectrum and the appearance of a strong sharp band at 3625 cm⁻¹ in the IR spectrum of the product. The latter value points to the absence of any intermolecular hydrogen bonding. This is due to the bulky nature of the substituents adjacent to the secondary OH group. Use of a 5.5 fold excess of ferrocene gave a product which appeared to be largely the bis complex from elemental analysis (Expt. 45). No product was obtained using equimolar quantities of ferrocene and arene (Expt. 47). A 10.8 fold excess of ferrocene gave mainly the tris complex (Expt. 46). The ¹³C spectrum of this product showed six closely grouped signals in the cyclopentadienyl range 74.8–77.7 ppm. The tris complex should exist in two isomeric forms (I and II).



All six cyclopentadienyl rings could, in principle, be magnetically non-equivalent which would explain the above

signal multiplicity. The crystal structure of tetracyclone¹⁷ shows it to be a propeller-shaped molecule where the dihedral (twist) angles between the phenyl substituents and the five-membered ring are greater for phenyl substituents remote from the CO group. ¹³C NMR studies have demonstrated that appreciable twist angles occur in solution,¹⁸ again the remoter phenyl substituents having larger twist angles. The sterically encumbered nature of the propeller structure considerably reduces the possibility of geometrical isomerism and we find no evidence for such isomers in the ¹³C NMR spectra of these complexes. Decacyclone (diacenaphtho[1',2'-j:1,2-]fluoroanthene) underwent complexation at the central ring. This



regiospecificity was clearly apparent from the ¹³C NMR spectrum of the product, which showed a single resonance at 95.79 ppm in the complexed arene region of the spectrum. The site of complexation is largely dictated by the electron density in the aromatic rings. Thus, for the extended polycyclic coronene, complexation was found to occur on the peripheral rings rather than the central ring.¹⁹ Extended Hückel model calculations

Table 4 Yields^a and reaction conditions for the synthesis of arylamine complexes [FeArNR₂(cp)][PF₆]^b using microwave dielectric heating^b

Expt. no.	Arylamine	Time (min)	Reagent ratios				Scale ^c	Yield (%)
			Arylamine	Ferrocene	AlCl ₃	Al		
49	PhNH ₂	5	1	1.7	3.2	4.6	0.065	44 (22) ^d
50	PhNH ₂	3	2	1	2	4	0.02	53
51	4-MeC ₆ H ₄ NH ₂	3	1	1	4	2.2	0.02	75 (58) ^e
52	1,2-(NH ₂) ₂ C ₆ H ₄	4	1	3	6	9	0.01	0
53	Ph ₂ NH	5	1	1	4	5.5	0.027	44 ^f (6) ^g
54	Ph ₂ NH	4	1	6	12	24	0.01	27 ^h
55	Ph ₃ N	4	1	1	4	5.6	0.027	67 ^f
56	Ph ₃ N	4	1	9	18	36	0.005	65 ^h
57	4-FC ₆ H ₄ NH ₂	4	1	1	2	4	0.06	35
58	4-ClC ₆ H ₄ NH ₂	2	1	1	2	4	0.02	19

^{a,b,c} As for Table 2. ^d Ref. 11. ^e Ref. 21. ^f Mono complex. ^g Ref. 9. ^h Bis complex.

Table 5 Yields^a of other [FeAr(cp)][PF₆]^b complexes prepared using microwave dielectric heating^b

Expt. no.	Arene	Time (min)	Reagent ratios				Scale ^c	Yield (%)
			Arene	Ferrocene	AlCl ₃	Al		
59	PhOMe	3	1	1	2	2	0.02	17 ^d (40–50) ^e
60	PhOSiMe ₃	3	2	1	2	4	0.01	5 ^d
61	PhCH ₂ OH	4	1	3	6	11	0.01	32
62	PhCHO	5	1	2	4	5.5	0.027	17 ^f
63	Ph ₂ CHOH	4	1	3	6	11	0.01	58
64	Ph ₂ CO	5	1	2	4	5.5	0.027	19 ^g
65	4-ClC ₆ H ₄ CHO	4	1	3	6	11	0.01	11 ^h
66	Ph ₃ P	3	1	1	2	2	0.01	30 ⁱ
67	Ph ₃ P	4	1	5	10	10	0.01	92 ^j
68	Ph ₃ SnCl	3	1	1	2	3.7	0.01	44 ^k
69	<i>N</i> -Phenylpyrrole	3	1	1.8	7	3.9	0.056	35
70	Na[BPh ₄]	3 ⁱ	1	2	4.8	7.4	0.005	42 ^k

^{a,b,c} As for Table 2. ^d Phenol complex. ^e Ref. 22. ^f Benzyl alcohol complex. ^g Benzhydrol complex. ^h 4-Chlorobenzyl alcohol complex. ⁱ 76% Mono, 24% bis complex. ^j 48% Mono, 52% bis complex. ^k Benzene complex. ^l Microwave setting high.

confirm that the latter has a lower charge density than the outer rings. Simple Hückel MO calculations have appeared²⁰ which predict that the central ring in decacyclene has a greater π electron density than the outer rings which is in accord with the observed regioselectivity described above.

(iii) Arylamine complexes

The microwave technique is particularly well suited to the synthesis of arylamine complexes (Table 4), excellent yields of simple aniline complexes being obtained. Thus a 75% yield of the *p*-toluidine complex was found even using a 1:1 ratio of amine to ferrocene (Expt. 51). We have, however, been unsuccessful in our attempts to prepare the phenylenediamine complex (Expt. 52). The reason for this is unclear but may be due to particularly strong coordination to the AlCl₃ thus denuding the aromatic ring of electron density. Both mono and bis complexes can be obtained from diphenylamine (Expts. 53, 54) and triphenylamine (Expts. 55, 56) simply by altering the amine to ferrocene ratio. Incorporation of extra functionality is also possible from 4-fluoro- and 4-chloroanilines (Expts. 57, 58) which are of value in the synthesis of aniline derivatives inaccessible by normal routes.

(iv) Miscellaneous complexes

The yields for a wide range of arenes appear in Table 5. Attempts to prepare the anisole complex resulted in demethylation to give a modest yield of the phenol complex (Expt. 59). This has previously been observed in the synthesis of the 2-methoxybiphenyl complex.²³ A similar result was obtained using trimethylsilyloxybenzene (Expt. 60). As expected, aryl

aldehydes and ketones always gave the alcohol complexes, again in modest yields (Expts. 62, 64, 65). The alcohol complexes themselves were obtained by ligand exchange in reasonably good yields when an excess of ferrocene was used.

Of particular interest were the complexes synthesized from triphenylphosphine. Some previous work has been done using this ligand, but details have not been published.²⁴ Under our microwave conditions, we were able to demonstrate that both mono and bis complexes can be made (Expt. 66, 67). Again the use of an excess of ferrocene is highly beneficial. The ³¹P NMR chemical shifts (rel. to 85% H₃PO₄) of these mono and bis complexes were -1.4 and -2.7 ppm, respectively. This compares with values for the free ligand and diphenylphosphinoferrrocene of -5.6 to -8²⁵ and -15.1 ppm,²⁶ respectively. Thus, the signals for the new complexes lie somewhat downfield from the ferrocene analogue which could reflect the electron-withdrawing nature of the [FeC₆H₅(cp)]⁺ moiety. However, this must remain speculative since ³¹P shifts are sensitive to small changes in hybridisation of the phosphorus atom.²⁷ Attempted complexation of chlorotriphenyltin resulted in considerable tin-carbon bond fission to give moderate yields of the benzene complex (Expt. 68). Normally, the complexed ring is less susceptible to electrophilic attack than the uncomplexed ring due to electron withdrawal by the [FeC₆H₅(cp)]⁺ group.²⁸ Presumably, in this case extra electron withdrawal by the chlorine substituent makes the tin atom much more susceptible to nucleophilic attack resulting in Sn-C bond fission. The tetraphenylborate ion also undergoes complexation with hydrolytic cleavage (Expt. 70). Here the boron atom can provide the electron density to the complexed

Table 6 Yield of *N*-phenylcarbazole from decomplexation of [Fe(η -*N*-phenylcarbazole)(η -cp)][PF₆] (1 g) using microwave dielectric heating^a in the presence of graphite (1 g)

A. Time(s)	60	90	120	150				
Yield (%) ^b	29	40	63	57				
Yield (%) ^c	46	65	96	36				
B. Wt. of graphite flakes (g)	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Yield (%) ^d	67	88	92	96	96	88	71	75

^a Microwave setting high. ^b Graphite powder. ^c Graphite flakes. ^d 2 min irradiation.

Table 7 Optimised yields of arene from microwave assisted^a decomplexation of various [FeAr(cp)][PF₆] complexes (1 g in each case)

Arene complex	Wt. of graphite flakes (g)	Yield (%)
Pentamethylbenzene	1.5	94
<i>N</i> -Phenylcarbazole	1.0	96
<i>N</i> -Phenylpyrrole	1.0	62
<i>N</i> ,2-Diphenylindole	2.0	71

^a 2 min microwave setting high.

phenyl group thus enhancing acid-catalysed cleavage. We have synthesised the tetraphenyl-borate complex by refluxing Na[BPh₄] with [(Fe(cp)(CO)₂)]I for 72 h in dry DME.²⁹ A value of 1.81 mm s⁻¹ was found for the quadrupole splitting obtained from the ⁵⁷Fe Mössbauer spectrum. This is considerably greater than the value for the benzene complex (1.68 mm s⁻¹)³¹ and is evidence of strong electron release to the [FeC₆H₅(cp)] group.

(v) Microwave-assisted decomplexation

Very recently we reported on the chemical decomplexation of [FeAr(cp)][PF₆] complexes.³² In addition to chemical methods, physicochemical techniques such as photolysis,¹² electroreduction³³ and pyrolytic sublimation³⁴ have been employed. In view of the thermal lability of the [FeAr(cp)]-[PF₆] complexes we decided to evaluate microwave heating as the method of decomplexation. In order to achieve the high temperatures (>200 °C) required for decomplexation, an efficient microwave coupler must be present. Carbon, in the form of graphite, is a very effective microwave absorber.³⁵ Accordingly, we studied the decomplexation of [Fe(η -*N*-phenylcarbazole)(η -cp)][PF₆]³⁶ under various conditions using either graphite flake or graphite powder. The results appear in Table 6. An intimate mixture of graphite and the complex was made prior to irradiation. The results showed this to be a rapid and efficient method of decomplexation. Graphite flake is better than the powder form, possibly because the larger surface area of the latter makes it a better heat conductor which may lead to some charring and loss of yield. The optimum conditions involve a 2 min irradiation using 1–2 g of graphite per gram of complex. Table 7 illustrates the method for a range of complexes.

Conclusions

The use of microwave dielectric heating, using a solid CO₂ condensing system in an ordinary domestic microwave oven, provides a simple and very rapid method of synthesising a wide range of [Fe(η -arene)(η -cp)][PF₆] complexes and should supersede conventional methods. In addition, decomplexation is also rapid and efficient with the use of graphite as the microwave coupler. A combination of these two techniques should prove a powerful tool for the synthetic chemist wishing to use iron sandwich complexes in the arylation of organic compounds.

Experimental

All the arenes used were commercially available and used without further purification. Reagent grade (98%) ferrocene, aluminium chloride and 1,2,4-trichlorobenzene were used in all the ligand exchange reactions. The aluminium powder employed was either 200 mesh (74 μ m) or 20 μ m particle size (Aldrich Chemical Co.) Graphite flake and powder (1–2 μ m) were purchased from Aldrich Chemical Co.

Microwave experiments were performed using a conventional domestic microwave oven (Sharp Easy Chef R5A53, 850 W), using the apparatus described in ref. 1. ¹H, ¹³C and ³¹P spectra were run using a JEOL EX270 spectrometer. Microanalyses were obtained in-house using a Perkin-Elmer, Series 2 CHN/O Analyser, Model 2400.

General synthetic method

The following large-scale preparation of the chlorobenzene complex is typical of the syntheses described in this work.

Synthesis of [Fe(η -C₆H₅Cl)(η -C₅H₅)] [PF₆]. Finely ground ferrocene (18.6 g, 0.1 mol), chlorobenzene (5.6 g, 0.05 mol) and aluminium powder (7 g, 0.26 mol) were added with stirring to 1,2,4-trichlorobenzene (15 cm³) in a 600 cm³ beaker. Finely ground AlCl₃ (26.6 g, 0.2 mol) was added to the mixture which was then stirred until it was homogeneous. A flanged beaker (400 cm³) containing solid CO₂ was placed over the reaction mixture and a small beaker of water (60 cm³) placed alongside the reaction vessel to absorb the excess of microwave radiation. The mixture was irradiated at a medium setting for 7 min and then allowed to cool. Ice (300 g) was carefully added in small portions to the mixture to decompose the excess of AlCl₃. The mixture was then returned to the microwave oven to be heated for a further 1 min in order to extract fully the complex as the water-soluble tetrachloroaluminate. As a precaution, the reaction beaker was placed on a large crystallising dish since frothing sometimes occurred which could cause a loss of product. The mixture was then gravity filtered and the filtrate washed twice with equal volumes of ether. After further filtration, the clear aqueous phase was treated with an aqueous NH₄PF₆ [60% HPF₆ (12.2 g, 0.05 mol) neutralised with conc. NH₄OH (8.1 g, 0.05 mol) in distilled water (25 cm³)]. The resultant flocculent green precipitate was filtered off through a sinter and washed with a small volume of PrⁱOH followed by ether; yield 9 g (48%). ¹H and ¹³C NMR spectra showed the crude product to be at least 95% pure. Purification was effected by filtering a solution of the crude product in CH₂Cl₂ into ether to give pure product (8 g, 43%).

All the syntheses described in this work followed the same procedure but with variations in irradiation time and solvent volume according to the scale of the reaction (Tables 2–5). In those cases where multiple complexation is possible, crude yields only are reported so that the composition of the products could be estimated from their ¹H and ¹³C NMR spectra. Analytical and spectroscopic data appear in Table 8.

Decomplexation

Owing to the high temperatures generated by absorption of microwave energy by graphite, the crucibles used for the

Table 8 ^{13}C NMR^{a,b} and analytical data for $[\text{Fe}(\eta\text{-arene})(\eta\text{-cp})][\text{PF}_6]$ complexes

Arene	Expt. no.	NMR spectroscopic data and analyses
PhCl	5	^{13}C : arene 108.14 (C-1), 89.85 (C-3,5), 89.38 (C-2,6), 88.38 (C-4). $\text{C}_5\text{H}_4\text{Me}$: 80.04 (C-2',5'), 79.03 (C-3',4'), 12.59 (Me). (Found: C, 36.75; H, 3.20. Calc. for: C, 36.72; H, 3.08%)
1,4- $\text{F}_2\text{C}_6\text{H}_4$	14	^{13}C : 137.46 (C-1,4), 80.48 (cp), 77.26 (C-2,3,5,6) $^1J_{\text{CF}}$ 273.9, $^2J_{\text{CF}}$ 18.6, $^3J_{\text{CF}}$ 3.7
1,2- ClFC_6H_4	15	^{13}C : 136.66 (C-2), 97.18 (C-1), 88.99 (C-6), 87.52 (C-5), 87.40 (C-4), 81.14 (cp), 79.66 (C-3) $^1J_{\text{CF}}$ 273.0, $^2J_{\text{CF}}$ 20.5, $^3J_{\text{CF}}$ 4.9
1,2-Me, FC_6H_4	17	^{13}C : 137.42 (C-1), 94.44 (C-2), 89.31 (C-3), 86.88 (C-4), 86.68 (C-5), 79.06 (cp), 78.00 (C-6), 14.78 (Me) $^1J_{\text{CF}}$ 270.5, $^2J_{\text{CF}}$ 16.3, 22.4, $^3J_{\text{CF}}$ 2.0, 6.8
1,3-Me, FC_6H_4	18	^{13}C : 138.25 (C-1), 103.93 (C-3), 87.41 (C-4), 86.48 (C-5), 79.15 (C-2), 78.70 (cp), 76.55 (C-6), 19.64 (Me) $^1J_{\text{CF}}$ 272.5, $^2J_{\text{CF}}$ 19.7, 21.0, $^3J_{\text{CF}}$ 6.8, 6.1
$\text{C}_6\text{H}_5\text{Br}$	20	^{13}C : 91.95 (C-2,6), 89.22 (C-3,5), 87.88 (C-4), 79.68 (cp) (Found: C, 31.3; H, 2.4. Calc. for: C, 31.2; H, 2.38%)
Ph_2CH_2^c Mono	24	^1H : 7.31s (2'-5'-H), 6.31s (2-5-H), 5.09 (cp), 4.06 (CH_2) ^{13}C : 139.51 (C-1'), 129.64, 129.52 (C-2',3',5',6'), 127.88 (C-4'), 107.94 (C-1), 89.19, 88.82 (C-2,3,5,6), 87.81 (C-4), 77.90 (cp), 41.06 (CH_2)
Ph_2CH_2^c Bis	25	^1H : 6.31s (2-5-H), 5.09s (cp), 4.14 (CH_2) ^{13}C : 103.14 (C-1), 88.02, 87.89 (C-2,3,5,6), 87.17 (C-4), 77.00 (cp), 38.30 (CH_2)
Ph_3CH^c Mono	26	^{13}C : 141.66 (C-1'), 128.97, 128.84 (C-2',3',5',6'), 127.27 (C-4'), 109.17 (C-1), 87.55, 87.33 (C-2,3,5,6), 86.74 (C-4), 76.61 (cp), 53.92 (CH)
Ph_3CH^c Bis	27	^1H : 7.50m (2'-6'-H), 6.40br s (3-5-H), 6.27br s (2,6-H), 4.88s (cp), 5.82s (CH) ^{13}C : 139.73 (C-1'), 129.08, 128.96 (C-2',3',5',6'), 128.35 (C-4'), 106.62 (C-1), 87.50 (C-4), 87.20, 87.00 (C-2,6), 86.91 (C-3,4), 76.56 (cp), 67.46 (CH)
(<i>E</i>) $\text{PhCH}=\text{CHPh}^c$ Bis	29	^1H : 7.47s ($\text{CH}=\text{}$), 6.66br s (3,5-H), 6.44br s (2,6-H), 6.38br s (4-H), 5.08s (cp) ^{13}C : 129.91 ($\text{CH}=\text{}$), 97.11 (C-1), 87.19 (C-3,5), 86.39 (C-4), 84.94 (C-2,6), 76.59 (cp)
<i>m</i> -Terphenyl ^c	32	^1H : 8.38s (2'-H), 8.16d (<i>J</i> 7.7, 4',6'-H), 7.78t (<i>J</i> 7.8, 5'-H) 6.98d (<i>J</i> 6.3, 2,6-H), 6.59t (<i>J</i> 6.0, 3,5-H), 6.48t (<i>J</i> 6.0, 4-H), 5.09s (cp) ^{13}C : 136.33 (C-1',3'), 130.47 (C-5'), 129.52 (C-4',6'), 126.98 (C-2'), 101.93 (C-1), 88.11 (C-3,5), 87.52 (C-4), 86.50 (C-2,6), 77.66 (cp) (Found: C, 44.5; H, 2.8. Calc. for: C, 44.13; H, 3.17%)
Acenaphthene	44	^{13}C : 150.71 (C-8), 135.14 (C-6), 124.63, 124.63 (C-5,7), 110.04 (C-1), 99.36 (C-8a), 97.14 (C-4a), 86.07 (C-3), 82.68, 81.88 (C-2,4), 77.04 (cp), 30.65 (C-9), 29.66 (C-10) (Found: C, 48.2; H, 3.8. Calc. for: C, 48.60; H, 3.60%) (Found: C, 49.5; H, 3.0. Calc. for: C, 51.0; H, 3.5%)
Tetracyclone Bis	45	(Found: C, 43.5; H, 2.9. Calc. for: C, 44.63; H, 3.14%)
Tetracyclone Tris	46	(Found: C, 43.5; H, 2.9. Calc. for: C, 44.63; H, 3.14%)
Decacyclone ^d	48	^{13}C : 129.64, 129.42 (C-2,4 etc), 126.44 (C-3 etc), 95.79 (C-1,2 etc), 82.28 (cp)
1,4-Me, $\text{NH}_2\text{C}_6\text{H}_4$	51	^{13}C : 125.10 (C-1), 96.38 (C-4), 87.10 (C-3,5), 77.21 (cp), 70.50 (C-2,6)
Ph_2NH	54	^1H : 6.58br s, 5.20s
Ph_3N	55	^{13}C : 143.58 (C-1'), 131.54 (C-3',5'), 128.91 (C-2',4',6'), 127.05 (C-1), 86.78 (C-3,5), 82.41 (C-4), 76.80 (cp), 70.30 (C-2,6)
Ph_3N	56	^{13}C : 140.98 (C-1'), 132.36 (C-3',5'), 131.62 (C-4'), 131.34 (C-2',6'), 128.95 (C-1), 87.58 (C-3,5), 85.71 (C-4), 79.59 (C-2,6), 77.92 (cp)
1,4-F, $\text{NH}_2\text{C}_6\text{H}_4$	57	^{13}C : 135.03 (C-1), 125.32 (C-4), 78.39 (cp), 76.20 (C-2,6), 67.92 (C-3,5) $^1J_{\text{CF}}$ 268.0, $^2J_{\text{CF}}$ 22.5, $^3J_{\text{CF}}$ 6.8
1,4-Cl, $\text{NH}_2\text{C}_6\text{H}_4$	58	(Found: C, 33.2; H, 2.8. Calc. for: C, 33.57; H, 2.82%)
Ph_2CHOH^c	63	^{13}C : 138.83 (C-1'), 128.61, 128.39 (C-2',3',5',6'), 126.78 (C-4'), 106.25 (C-1), 87.78, 87.44 (C-2,3,5,6), 86.35 (C-4), 76.79 (CH), 76.50 (cp) (Found: C, 47.8; H, 3.2. Calc. for: C, 48.03; H, 3.80%)
Ph_3P Mono	66	^{13}C : 136.84 (C-1'), 135.00 (C-2',6'), 131.22 (C-4'), 130.10 (C-3',5'), 99.21 (C-1), 91.04 (C-2,6), 89.37 (C-3,5), 88.72 (C-4), 78.86 (cp) $^1J_{\text{PC}}$ -24.5, -22.5, $^2J_{\text{PC}}$ 21.5, 14.8, $^3J_{\text{PC}}$ 7.7, 4.9 ^{31}P : -1.45 (P), -142.18 (PF_6), $^1J_{\text{PF}}$ = 711.4
Ph_3P Bis	67	^{31}P : -2.68
$\text{PhC}_4\text{H}_4\text{N}$	69	^{13}C : 120.82 (C-2',5'), 113.89 (C-3',4'), 88.31 (C-3,5), 87.04 (C-4), 79.43 (C-2,6), 78.62 (cp) (quaternaries C-1, C-1' not observed)

^a Solvent [$^2\text{H}_6$]acetone unless otherwise stated. ^1H , ^{13}C shifts (δ) are relative to TMS. ^{31}P shifts are relative to 85% H_3PO_4 using the downfield positive convention, s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. *J* Values are given in Hz. ^b Where complexed and uncomplexed aromatic rings are both present, the atoms in the latter are denoted with primes. ^c [$^2\text{H}_6$]-DMSO. ^d Numbering as indicated in text.

pyrolyses were insulated from the main reaction beaker by a layer of Kao wool. Failure to do so caused the beaker to crack after about 2 min on a high setting. The following example illustrates the method.

Decomplexation of $[\text{Fe}(\eta\text{-}N\text{-phenylcarbazole})(\eta\text{-cp})][\text{PF}_6]$. The $\eta\text{-}N\text{-phenylcarbazole}$ complex (1 g, 1.96 mmol) was thoroughly mixed with graphite flakes (1 g) in a small porcelain crucible (15 cm^3) equipped with a lid. The crucible was then

placed in a reaction beaker (600 cm^3) layered with Kao wool. The lid was placed on the crucible and the 'cold finger' filled with solid CO_2 set in place. The whole was microwaved for 2 min on a high setting. On cooling, the mixture was extracted with ether (3 \times 10 cm^3). The combined extracts were filtered and evaporated to give a solid (0.46 g, 96%) which had a melting point (95 $^\circ\text{C}$) identical with that of an authentic sample of *N*-phenylcarbazole.

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