Decomplexation of (η-Arene)(η-cyclopentadienyl)iron(II) Hexafluorophosphates: a Convenient One-pot Arylation Procedure

Richard A. Brown, Sharon I. S. Fernando and Roger M. G. Roberts*
Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK

A study has been made of the relative merits of a range of decomplexation reagents in the demetallation of [(η-arene)(η-cyclopentadienyl)Fe][PF_6] salts. 1,8-Phenanthroline gave good yields of the free ligand when simple arene complexes were used but did not demetallate more sterically hindered species. The reaction was found to be light sensitive. Bipyridine gave much lower yields. Potassium *tert*-butoxide in pyridine or DMSO was found to be an excellent demetallating agent even with sterically crowded complexes. A one-pot arylation procedure was developed and extended to include a number of important heterocyclic derivatives. The mechanism of these decomplexation reactions is briefly addressed.

Organometallic compounds have long been used in synthetic organic chemistry. In recent years, much effort has been devoted to the synthesis of arene complexes of transition metals since complexation profoundly alters the reactivity of the arene.[1] One of the most studied systems has been the arene complexes of chromium,[2] [(η-arene)$(CO)_3$Cr], particularly with respect to their role in modifying the arene moiety.[3] There are, however, a number of drawbacks to using these complexes on a large scale, namely (a) the starting material, $Cr(CO)_6$, is expensive, (b) synthesis of the complexes involves rather long reaction times and (c) certain reactive substituents such as NO_2 and CHO undergo unwanted side-reactions. The arene complexes of other transition metals such as Mn, Ru, Os, Mo and W are known but have not been extensively investigated as intermediates for organic synthesis mainly due to one or more of the drawbacks listed above.

The arene complexes of iron[4,5] have none of these disadvantages and can be very readily prepared in high yield. The [(η-arene)(η-cyclopentadienyl)Fe][PF_6] salts ([ArCpFe][PF_6]) are particularly attractive in this context since halogen[6] and nitro[7] substituents on the arene can be readily displaced by a variety of nucleophiles in S_NAr type reactions. However, the use of [ArCpFe] complexes as arylating agents depends on there being an efficient method of removing the resulting modified arene from the complex. There have been numerous attempts to establish a convenient demetallation procedure over the last two decades. A range of useful methods have been recently developed by Sutherland's group. Thus, conversion of the [ArCpFe] salts into their cyclohexadienyl counterparts by nucleophilic reagents followed by oxidation with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) results in good yields of the modified arene in certain cases.[8] However, the method suffers from the restriction that the cyclohexadienyl intermediate complexes are difficult to prepare when electron-releasing substituents are present on the arene ring. Photolytic[9] and electroreductive[10] techniques have also been used with some success.

Probably the most widely used method of decomplexation is that of pyrolytic sublimation.[11] This technique can only be used where the product arene is thermally stable. Since photolysis, pyrolytic sublimation and electroreduction require rather specialised apparatus, we decided to look for simple chemical methods of arene cleavage. Shortly after the discovery of the [ArCpFe] sandwich complexes, Nesmeyanov[12] observed that considerable decomposition occurred when attempting the displacement of chlorine in [(C_6H_5Cl)CpFe][PF_6] by a hydroxide ion. This has led us to investigate the use of strongly basic media to effect demetallation. In addition, earlier reports of decomplexation using bidentate ligands[13] prompted us to explore the possibility of using strong iron ligators such as 1,8-phenanthroline as cleavage agents. In this paper we compare the relative efficiencies of the bidentate and strongly basic cleavage agents and present a convenient one-pot method for the synthesis of modified arenes.

Results and Discussion

Arene Cleavage using 1,8-*Phenanthroline and Bipyridine.*—The decomplexation by these reagents was carried out in refluxing pyridine using a 1:3 mol ratio of complex to cleavage reagent. The decomplexations were carried out under various conditions and the results appear in Table 1. The reaction with phenanthroline is sensitive to light as shown by the finding that over 90% yield of *p*-xylene in 3 h was obtained from the corresponding complex when illuminated whereas only a 9% yield occurred in the dark. As expected, heavily methylated arene complexes such as durene did not react. This is due to inhibition of the chelating effect of the phenanthroline by the bulky methyl substituents. Generally, phenanthroline was a significantly better demetallating agent than bipyridine. The results for the chlorinated arenes are interesting. The *ortho* dichlorobenzene complex is more readily cleaved than its *para* dichlorobenzene counterpart. The incoming bidentate ligand finds relatively easy access to the central iron atom in the former by approaching from the side remote from the two chlorine substituents, whereas in the latter case the chlorine atoms inhibit approach from all directions.

Arene Cleavage using Strongly Basic Media.—No such inhibition was found with Bu^{t}OK as the decomplexation agent. A 68% yield of durene was obtained from [(η-1,2,4,5-tetramethylbenzene)(η-Cp)Fe][PF_6] and Bu^{t}OK in refluxing pyridine (3 h). Similarly a 93% yield of *p*-dichlorobenzene was obtained from the parent complex under the same conditions.

Demetallations using Bu^{t}OK in DMSO also worked well (Table 2). BuLi can also be used but this results in lower yields, presumably as a result of ion pairing of the $LiCH_2SOCH_3$ formed in the reaction.[14]

Room temperature demetallations using Bu^{t}OK show no radical characteristics and the reactions can be monitored by ^1H and ^{13}C NMR spectroscopy. The ease of arene cleavage depends on the nature of the arene, the base and the solvent. For

Table 1 Yields (%) of arene obtained from demetallation of [(η-arene)(η-Cp)Fe][PF_6] salts using 1,8-phenanthroline (phen), bipyridine (bpy) and potassium *tert*-butoxide

		Reaction time[b] (h)				
Arene	Cleavage agent[a]	0.17	0.5	1.0	2.0	3.0
p-Xylene	phen	—	—	73	89	93
p-Xylene[c]	phen	7	39	70	78	91
p-Xylene[d]	phen	0	0	2	8	9
p-Xylene	bpy	—	—	20	24	30
p-Xylene	Bu^{t}OK	—	—	72	75	91
Durene	phen	—	—	0	0	0
Durene	Bu^{t}OK	—	—	0	21	68
Chlorobenzene	phen	—	—	91	95	95
Chlorobenzene	Bu^{t}OK	—	—	21	72	90
o-Dichlorobenzene	phen	—	—	19	63	84
o-Dichlorobenzene	bpy	—	—	12	24	32
o-Dichlorobenzene	Bu^{t}OK	—	—	7	83	86
p-Dichlorobenzene	phen	—	—	7	15	28
p-Dichlorobenzene	Bu^{t}OK	—	—	10	88	93

[a] mol ratio of [ArCpFe][PF_6] to cleavage agent is 1:3, phen = 1,8-phenthroline, bpy = bipyridine. [b] In refluxing pyridine. [c] Irradiation with 100-W lamp. [d] Reaction conducted in dark.

Table 2 Demetallation of [(η-arene)(η-Cp)Fe][PF_6] salts in basic media

Arene	Base[a]	Solvent	Temp. (°C)	Reaction time[a] (h)	Yield (%)
Fluorobenzene	Bu^{t}OK	Pyridine	115	1	60
o-Xylene	Bu^{t}OK	Pyridine	115	1	52
N,N-Dimethylaniline	Bu^{t}OK	Pyridine	115	1	70
N-Butylaniline	Bu^{t}OK	Pyridine	115	1	61
N-(1-Phenylethyl)aniline	Bu^{t}OK	Pyridine	115	1	70
N-(Butyl)-2-chloroaniline	Bu^{t}OK	Pyridine	115	1	75
N-(1-Phenylethyl)-2-chloroaniline	Bu^{t}OK	Pyridine	115	1	80
1-Phenylindole	BuLi[b]	DMSO	20	2	63
1-Phenyl-1*H*-benzotriazole	BuLi[c]	DMSO	20	2	26
1-Phenyl-1*H*-benzotriazole	BuLi[c]	DMSO	20	48	48
1,2-Di(1*H*-benzotriazolyl)benzene	Bu^{t}OK[d]	DMSO	20	17	20
9-Phenyl-9*H*-carbazole	Bu^{t}OK[c]	DMSO	20	1	83
9-Phenyl-9*H*-carbazole	BuLi[b]	DMSO	20	2	38
9-Phenyl-9*H*-carbazole	BuLi[b]	DMSO	20	17	93
N-Phenyladenine	Bu^{t}OK[c]	Pyridine	20	48	22
N-Phenyladenine	BuLi[b]	DMSO	20	17	9

[a] Three-fold excess over complex unless otherwise stated. [b] Equimolar base. [c] Two-fold excess base. [d] Five-fold excess base.

Bu^{t}OK, both benzene and fluorobenzene complexes decomplex almost completely after 2 h in [$^2H_6$]-DMSO with no deuterium incorporation in the products. However, the chlorobenzene complex behaves differently. Equilibration with Bu^{t}OK for 1 h causes no decomplexation. (Indeed, no decomplexation was observed after 24 h.) Both ^1H and ^{13}C NMR spectra (Fig. 1) reveal the presence of two quite separate Cp signals. The downfield resonance of the two in each case is that of unchanged chlorobenzene complex. Examination of the ^1H spectrum shows that 2,6-H signal at 6.74 ppm has a significantly reduced intensity due to H/D exchange. This probably occurs *via* the following equilibria, as shown in Scheme 1.

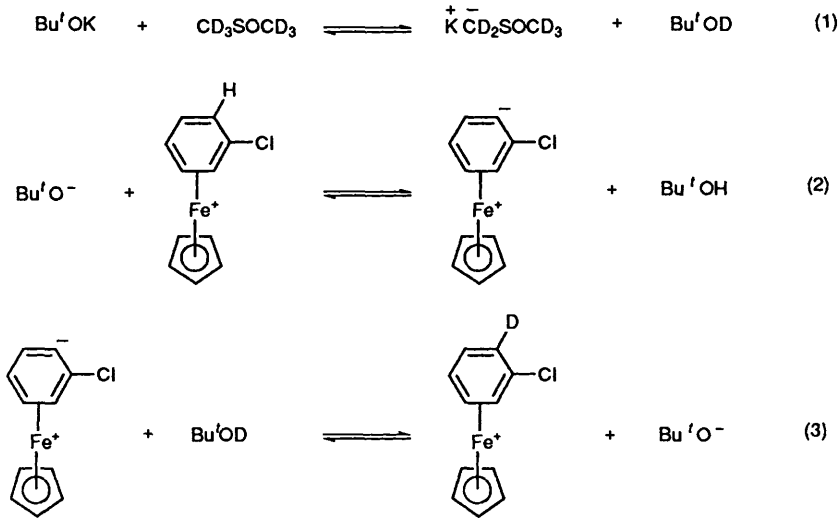
Exchange appears to be specific to the 2(6)-positions and is probably caused by the acidity-enhancing nature of the adjacent chlorine substituent. The Fe^+Cp moiety will also increase the acidity of the ring hydrogens. Interestingly, neither the benzene or fluorobenzene released from their parent complexes shows any deuterium incorporation, suggesting that decomplexation is faster than exchange for these substrates. Change of base from potassium butoxide to sodium methoxide also has a profound effect. NaOMe in [$^2H_6$]-DMSO causes extensive decomplexation after 30 min liberating chlorobenzene which shows no deuterium incorporation. No anisole is observed which precludes any chloride displacement by OMe. This is in direct contrast to the results obtained by Knipe[15] using solvent methanol where S_NAr displacement was the dominant process. Clearly the nature of the solvent also has an important effect on the promotion of decomplexation.

The second species present in the spectra for the Bu^{t}OK reaction, shown in Fig. 1, is the *tert*-butoxybenzene complex [(η-C_6H_5O-Bu^t)(η-Cp)Fe][PF_6] (confirmed by comparison with an authentic sample prepared by refluxing the chlorobenzene complex with Bu^{t}OK in Bu^{t}OH). This complex also shows H/D exchange of 2,6-H (4.89 ppm). ^{57}Fe Mössbauer parameters of the frozen reaction solution support the above identification. Quadrupole splitting (1.77 mm s^{-1}) and isomer shift (0.51 mm s^{-1}) are close to those found for the anisole complex[16] (1.76 and 0.52 mm s^{-1}, respectively).

The strikingly deep mauve solutions of the chlorobenzene complex with Bu^{t}OK in DMSO is redolent of those reported by Sutherland[17] in his work on deprotonation of alkylbenzene complexes to form zwitterionic species.

Unfortunately, no NMR data is available for NaC_6H_5 or KC_6H_5 from which comparisons can be made. In any case the standing concentration of the zwitterion is likely to be low.

The absence of demetallation in the case of the chlorobenzene complex with Bu^{t}OK could be due to a relatively higher concentration of the zwitterionic intermediate caused by carb-



Scheme 1

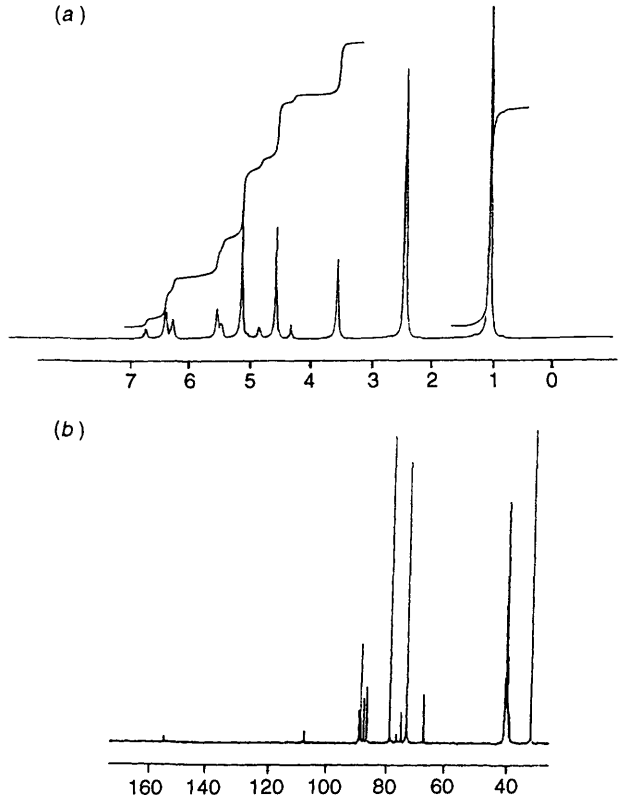


Fig. 1 (*a*) ^1H NMR spectrum of a reaction solution of [(η-C_6H_5Cl)-(η-Cp)Fe][PF_6] (0.5 mol dm^{-3}) and potassium *tert*-butoxide (0.75 mol dm^{-3}) in [$^2H_6$]-DMSO after 45 min. (*b*) ^{13}C NMR spectrum of the same reaction solution.

anion stabilisation by the inductive effect of the neighbouring chlorine substituent. The resultant negatively charged arene would discourage any direct displacement of the ligated arene by the *tert*-butoxide ion. Such a mechanism would be the nucleophilic counterpart of the $AlCl_3$-catalysed ligand exchange[18] used to synthesise the [ArCpFe][PF_6] complexes. However, in the light of the observed rapid decomplexation by methoxide ion, we incline to the view that steric effects are dominant, resulting in S_NAr displacement of the chlorine by the *tert*-butoxide ion rather than ligand cleavage which would be sterically more demanding.

The results of these low-temperature cleavages appear in Table 2 where the above method has been extended to include a number of heterocyclic derivatives.

At higher temperatures (100 °C) decomplexation is accompanied by the formation of significant amounts of phenylferrocene and 1,3-diphenylferrocene in addition to ferrocene itself. The presence of 1,3-diphenylferrocene, in particular, combined with the observation that no reaction occurs when a radical inhibitor is present, points to a radical process under these conditions. A useful variant of the above method is the use of refluxing pyridine as the reaction medium. This results in excellent yields (Table 2) and has the advantage that the solvent is much more easily removed.

We have made use of the above findings to develop a one-pot arylation procedure. Equilibration of [(η-C_6H_5Cl)(η-Cp)Fe]-[PF_6] with $BuNH_2$ in pyridine at room temperature for 15 min results in the formation of [(η-C_6H_5NHBu)(η-Cp)Fe][PF_6]. The product was not isolated but the solution was then treated with three equivalents of Bu'OK and refluxed for 1 h. On work-up a yield of 80% of *N*-phenylbutylamine was obtained. The results of this and other arylations appear in Table 3. For the heterocyclic derivatives, deprotonation must be effected before reaction with the chlorobenzene complex (see Experimental section). Table 3 shows the wide applicability of this one-pot procedure which should prove of value as a general method of arylating N, O and S substituted organic compounds.

Experimental

AnalaR pyridine was dried over KOH pellets and stored over molecular sieves (4Å). HPLC grade DMSO was used and stored over molecular sieves. Potassium *tert*-butoxide (Aldrich Chemical Co. Ltd.) was of reagent grade quality (95%) and was stored over P_2O_5 in a desiccator. [(η-Chlorobenzene)-(η-cyclopentadienyl)iron] and [(η-1,2-dichlorobenzene)(η-cyclopentadienyl)iron] hexafluorophosphates were prepared using standard ligand-exchange reactions.[19] The synthesis of the heterocyclic complexes forms the basis of a prior report.[20] The products of demetallation were characterised by ^1H and ^{13}C NMR using a JEOL EX270 spectrometer. The following numbering schemes are used for the *N*-phenyl heterocycles, as shown in Fig. 2.

Assignments were made by reference to data in the review by Begtrup and Elguero.[21] Samples were run in $CDCl_3$ unless otherwise stated.

Decomplexation of [(η-Arene)(η-Cp)Fe][PF_6] *Complexes with* 1,8-*Phenanthroline.*—The [ArCpFe][PF_6] salt (1.0 mmol)

Table 3 Yields from one-pot arylation reactions using [(η-chlorobenzene)(η-Cp)Fe][PF_6] (A) and [η-(1,2-dichlorobenzene)(η-Cp)Fe][PF_6] (B) as arylating agents

Nucleophilic reagent	[ArCpFe][PF_6]	Base	Solvent	Temp. (°C)[a]	Reaction time (h)	Yield (%)
Butylamine	A	Bu^{t}OK	Pyridine	115 (20)	1 (0.2)	80
(±)-α-Methylbenzylamine	A	Bu^{t}OK	Pyridine	115 (20)	1 (0.2)	65
4-Aminobutanol	A	Bu^{t}OK	Pyridine	115 (20)	1 (0.2)	75
Butylamine	B	Bu^{t}OK	Pyridine	115 (20)	1 (0.2)	74
4-Aminobutanol	B	Bu^{t}OK	Pyridine	115 (20)	1 (0.2)	86
1*H*-Indole	A	Bu^{t}OK (KOH)	DMSO	20 (20)	2 (1)	85
1*H*-Benzotriazole	A	Bu^{t}OK (KOH)	Pyridine	20 (20)	17 (1)	5[b]
9*H*-Carbazole	A	Bu^{t}OK (KOH)	Pyridine	20 (20)	48 (1)	12
Tryptamine	A	Bu^{t}OK (KOH)	Pyridine	20 (20)	48 (1)	33[c]

[a] The figures and reagent in parentheses refer to the formation of the intermediate complex. Those not in parentheses refer to the demetallation process. [b] 1-Phenyl-1*H*-benzotriazole was separated from the 2*H*-isomer by column chromatography. [c] The ^{1}H-*N*-phenyl and ω-*N*-phenyl isomers were formed in equal amounts.

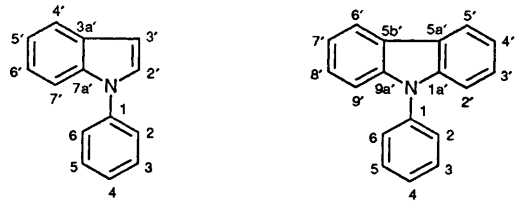


Fig. 2

was dissolved in dry pyridine (20 cm^3) and 1,8-phenanthroline (3.0 mmol) was added to the solution which was then refluxed for the desired period of time. After cooling, the red reaction solution was added to ether (100 cm^3) and the red precipitate of [Fe(phen)$_3$][PF_6] filtered off. The ether was removed by rotary evaporation at room temperature. The resultant pyridine solution was analysed by GLC using a Perkin-Elmer F17 Gas Chromatograph using Silicone SE30 (10%) on Chromosorb W (80–100 mesh) and a series of standards for the liberated arenes. The results appear in Table 1. A similar procedure was adopted for demetallation by bipyridine.

Decomplexation of [(η-Arene)(η-Cp)Fe][PF_6] *Complexes with Potassium* tert-*Butoxide.*—The following procedure is a typical example of these cleavages. [(η-*N*-Butylaniline)(η-Cp)Fe][PF_6] (1.0 g, 2.41 mmol) was dissolved in dry pyridine (20 cm^3) and Bu^{t}OK (0.81 g, 7.24 mmol) added to the mixture which was then refluxed for 1 h. The cooled solution was poured into ether (100 cm^3) and the resultant precipitate filtered off. Evaporation of the filtrate gave a tan oil (0.22 g, 61%) (Found: C, 80.1; H, 9.6. Calc. for $C_{10}H_{15}N$: C, 80.4; H, 10.0%); δ_H(ext. TMS) 1.23 (t, CH_3), 1.80 (m, CH_2), 2.42 (q, CH_2), 3.33 (m, CH_2), 6.84 (d, 2,6-H), 7.02 (t, 4-H), 7.13 (d, 3,5-H); δ_C(ext. TMS) 13.61 (CH_3), 20.02 (CH_2), 31.38 (CH_2), 43.33 (CH_2), 112.38 (C-2,6), 116.65 (C-4), 128.86 (C-3,5) and 148.70 (C-1).

The following compounds were prepared using the above method, the yields appearing in Table 2.

1-(1-*Phenylethyl*)*aniline.* (Found: C, 84.5; H, 8.2. Calc. for $C_{14}H_{15}N$: C, 85.2; H, 7.6%); δ_H 1.20 (d, CH_3), 4.00 (q, CH), 6.4–7.4 (m, 10 ArH) and 8.32 (s, NH); δ_C 24.78 (CH_3), 51.15 (CH), 113.20 (C-2,6), 117.08 (C-4), 126.68 (C-2′,5′), 128.34 (C-4′), 128.41, 128.96 (C-3, C-3′, C-5,5′), 145.11 (C-1′), 147.19 (C-1). (Primed numbers refer to the phenyl group.)

1-*Butyl*-2-*chloroaniline.* δ_H 1.21 (t, CH_3), 1.82 (m, CH_2), 2.29 (q, CH_2), 3.39 (m, CH_2), 6.52 (d, 6-H) and 6.7–7.2 (m, 3-, 4-, 5-H); δ_C 13.76 (Me), 20.18 (CH_2), 31.25 (CH_2), 112.52 (C-6), 116.64 (C-4), 123.61 (C-2), 127.63, 128.89 (C-3, -5) and 149.66 (C-1).

1-(1-*Phenylethyl*)-2-*chloroaniline.* δ_H 1.35 (d, CH_3), 4.06 (q, CH), 6.4–7.3 (m, 9 ArH) and 8.59 (br s, NH); δ_C 21.78 (CH_3), 50.39 (CH), 113.17 (C-6), 117.21 (C-4), 118.92 (C-2), 124.21 (C-2′, -6′), 127.21, 128.91, 129.37 (C-2, -5, -4′), 129.97 (C-3′, -5′), 143.12 (C-1′) and 151.72 (C-1).

One-pot Synthesis.—A typical procedure is described for the *N*-phenylation of 2-aminobutanol. [(η-Chlorobenzene) (η-Cp)Fe][PF_6] (1.0 g, 2.65 mmol) was dissolved in dry pyridine and 2-aminobutan-1-ol (0.47 g, 5.3 mmol) added to the solution which was then stirred for 10 min. Bu^{t}OK (0.89 g, 7.9 mmol) was then added to the mixture which was refluxed for 1 h and, after cooling, was poured into ether (100 cm^3). The resulting precipitate was filtered off and the filtrate rotary evaporated to yield 2-anilinobutan-1-ol as a light brown oil (0.17 g, 75%) (Found: C, 72.1; H, 8.7. Calc. for $C_{10}H_{15}NO$: C, 72.7; H, 9.1%); δ_H 0.99 (t, CH_3), 1.64 (m, CH_2), 3.4 and 3.8 (m, CH_2, CH), 6.68 (d, 2-, 6-H), 6.92 (br s, 4-H), 7.01 (br s, 3-, 5-H) and 8.62 (br s, NH); δ_C 17.72 (CH_3), 21.91 (CH_2), 39.27 (CH_2), 53.20 (CH), 112.97 (C-2, -6), 119.23 (C-4), 127.39 (C-3, -5) and 150.09 (C-1).

2-(2′-Chloroanilino)butan-1-ol was prepared in 86% by the same route; δ_H 0.77 (t, CH_3), 1.56–1.62 (m, CH_2), 3.21–3.97 (m, CH_2, CH) 6.7–7.0 (br s, ArH) and 8.42 (s, NH); δ_C 16.71 (CH_3), 20.17 (CH_2), 41.91 (CH_2), 51.30 (CH), 112.21 (C-6), 118.20 (C-4), 118.27 (C-2), 127.71 (C-5) and 129.23 (C-3).

Heterocyclic Derivatives.—Typical procedures are described below for demetallation of the heterocyclic complexes.

Cleavage of [(η-1H-N-*Phenyladenine*)(η-Cp)Fe][PF_6] *using Bu^{t}OK.* Potassium *tert*-butoxide (0.19 g, 1.68 mmol) and the adenine complex (0.40 g, 0.84 mmol) were stirred in dry pyridine (5 cm^3) for 48 h. The pyridine was removed by rotary evaporation and the crude product was chromatographed on neutral alumina eluting with CH_2Cl_2. The major band yielded 1*H*-*N*-phenyladenine (0.04 g, 22%) as a light brown solid (Found: C, 62.2; H, 4.3; N, 33.2. Calc. for $C_{11}H_9N_5$: C, 62.55; H, 4.29; N, 33.16); δ_C 119.50 (C-3a′), 123.00 (C-2, -6), 129.56 (C-3, -5), 127.46 (C-4), 139.66 (C-2′), 149.31 (C-9a′), 153.29 (C-6′) and 156.53 (C-4′).

The above procedure was modified slightly for reactions in DMSO. The reaction solution was quenched in water and the organic product extracted with CH_2Cl_2. After the CH_2Cl_2 extract had been concentrated it was chromatographed as before. The following derivatives were obtained using this modification.

9-*Phenyl*-9H-*carbazole.* δ_C 109.62 (C-2′), 119.78 (C-4′), 120.13 (C-5′), 123.23 (C-5a′), 125.80 (C-3′), 126.94 (C-2), 127.46 (C-4), 129.71 (C-3), 137.56 (C-1) and 140.74 (C-1a′).

1,2-*Bis*(1H-*benzotriazolyl*)*benzene.* δ_C 110.15 (C-7′), 120.31 (C-4′), 125.06 (C-5′), 129.13 (C-3), 129.13 (C-3) and 129.19 (C-4).

Identification of Phenylferrocenes from Reactions in DMSO at 100 °C.—Potassium hydroxide (0.30 g, 5.4 mmol) was stirred in DMSO (20 cm^3) at 80–100 °C for 5 min whilst carbazole (0.30 g, 1.8 mmol) was added to it. The orange solution was stirred at 100 °C for 2 h after which [(η-C_6H_5Cl)(η-Cp)-Fe][PF_6] (1.36 g, 3.6 mmol) was added to the reaction mixture which was then irradiated with a 100-W tungsten lamp for a further 2 h at 100 °C; it was then left overnight to cool. The dark reaction mixture was poured into ether (150 cm^3) and the whole filtered. The ethereal layer was separated, washed with dil. HCl (3 × 100 cm^3) and water (2 × 100 cm^3), dried and concentrated by rotary evaporation. The residue was then chromatographed on neutral alumina using hexane–ethanol (2:1) as the eluent. This separated the ferrocenes from the remaining products. After evaporation of the eluent a golden orange oil was obtained which was rechromatographed on acidic alumina with hexane as eluent. Two major components were separated and identified as phenylferrocene (5%) and 1,3-diphenylferrocene (5%) from their ^{13}C NMR spectra in [$^2H_6$]acetone.[22]

(a) *Phenylferrocene*: δ_C 67.10 (C-2′, -5′), 69.64 (C-3′, -4′), 70.20 (Cp), 126.60 (C-4), 126.78 (C-2, -6) and 129.10 (C-3, -5); (b) 1,3-*diphenylferrocene*: 65.70 (C-2′), 67.98 (C-4′, -5′), 71.83 (Cp), 87.05 (C-1′, -3′), 126.83 (C-2, -4, -6), 129.16 (C-3, -5) and 139.92 (C-1).

Preparation of [(η-$C_6H_5OBu^t$)(η-Cp)Fe][PF_6].—A slurry of [(η-C_6H_5Cl)(η-Cp)Fe][PF_6] (0.82 g, 2.0 mmol) in *tert*-butyl alcohol (15 cm^3) was treated with potassium *tert*-butoxide (0.25 g, 2.2 mmol) and the whole refluxed for 2 h with vigorous stirring. The mixture was filtered whilst still hot into Et_2O (100 cm^3). The resultant orange–brown solid was filtered off, washed with Et_2O and air dried; yield 0.05 g, (6%); δ_C([$^2H_6$]-DMSO) 31.33 (CH_3), 67.08 [$C(CH_3)_3$], 73.13 (Cp), 75.18 (C-2, -6), 86.25 (C-3, -4, -5) and 153.12 (C-1).

Reactions in [$^2H_6$]*Dimethyl Sulfoxide.*—[(η-C_6H_5Cl)(η-Cp)Fe][PF_6] (0.40 g, 1.0 mmol) was dissolved in [$^2H_6$]-DMSO (2 cm^3) and Bu^tOK (0.12 g, 1.1 mmol) was added to the solution. The whole was shaken and then set aside for 1 h to give a deep mauve mixture. This was gravity filtered and the ^1H and ^{13}C NMR spectra obtained for the resultant solution (Fig. 1).

Mössbauer Spectroscopy.—^{57}Fe Mössbauer spectra were run and fitted as described previously.[23]

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