

Studies on nucleophilic substitution reactions with cyclopentadienyliron complexes of some chloroarenes and nitroarenes and syntheses of substituted arenes by demetallation of the substitution products

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Abstract

Nucleophilic substitution reactions with the cyclopentadienyliron (CpFe) complex of *m*- or *p*-dichlorobenzene with carbanion nucleophiles derived from ethyl acetoacetate (EAA), dibenzoylmethane (DBM) or diacetylmethane (DAM) were found to give only monosubstitution as previously observed for the CpFe complex of *o*-dichlorobenzene. Reaction of the CpFe complex of 2,6-dimethylchlorobenzene (XIVa) or 2,6-dimethylnitrobenzene (XIVb) with nucleophiles derived from ammonia, dimethylamine, *n*-butylamine, pyrrolidine, ethanol, phenol, *o*-thiocresol and EAA all gave S_NAr products, without significant steric hindrance. However, no reaction was observed in the treatment of XIVa or XIVb with DBM, suggesting that only with a bulky nucleophile such as that derived from DBM were steric hindrance effects sufficiently large to prevent an S_NAr reaction with XIVa or XIVb. Pyrolytic sublimation of the various S_NAr products was found to cause decomposition in some cases, but in most instances, demetallation took place giving rise to substituted arenes. New substituted arenes prepared in this way in the present work included $RC_6H_4CH(COC_6H_5)_2$, with R = *p*-CH₃, *o*-Cl, *m*-Cl or *p*-Cl, and 2,6-(CH₃)₂C₆H₃Y, with Y = CH₃(CH₂)₃NH, C₂H₅O or *o*-CH₃C₆H₄S.

Introduction

Among the earliest examples of a nucleophilic substitution on an organometallic system was the work of Nicholls and Whiting [1] on the reaction of η^6 -chlorobenzene-tricarbonylchromium with NaOCH₃ in CH₃OH to give η^6 -anisole-tricarbonylchromium. Subsequently, extensive work has been done on substitution and addition reactions, and their synthetic applications, with arenes complexed to the tricarbonylchromium or tricarbonylmanganese moiety, the early literature having

been reviewed by Semmelhack [2,3] and by Jaouen [4]. More recent examples of organic synthesis via nucleophilic substitution reactions with tricarbonylchromium or tricarbonylmanganese complexed haloarenes are the work of Pearson and co-workers [5] and Alemagna and coworkers [6]. In his 1976 review, Semmelhack [2] pointed out that while chlorobenzene complexed to cyclopentadienyliron (CpFe) showed a significantly stronger activating effect than a *p*-nitro substituent, important applications of such CpFe complexes required further studies on the range of nucleophiles that would give efficient addition and/or substitution reactions. In the past decade, extensive studies on both addition and substitution reactions with CpFe complexes have been carried out. Among these studies was the demonstration that the CpFe complexed chlorobenzene was much more reactive than the corresponding tricarbonylchromium complexed chlorobenzene, for example, by a factor of about 10^5 in the nucleophilic substitution reaction with the methoxide ion [7,8]. Further studies on nucleophilic substitution reactions with CpFe complexed systems will be discussed in the present paper.

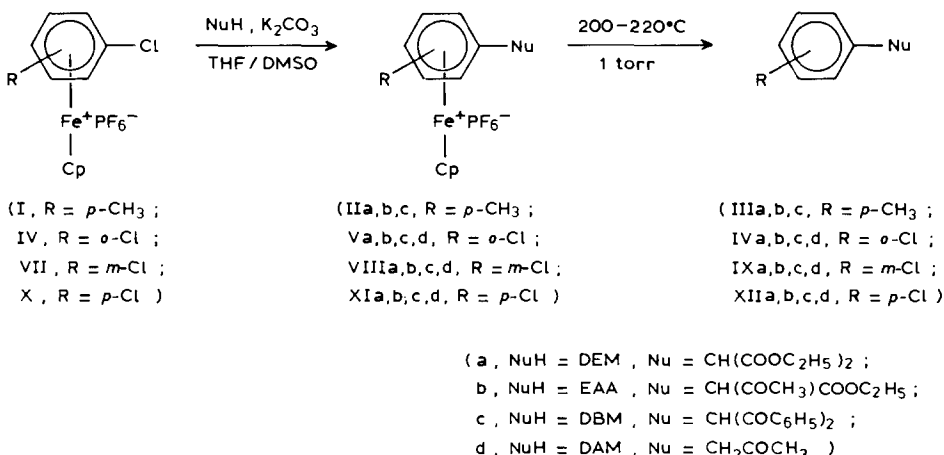
The displacement of the chloride ion from the η^6 -chlorobenzene- η^5 -cyclopentadienyliron cation by a number of nucleophiles was first reported by Nesmeyanov and coworkers [9,10]. A similar displacement reaction with the hydroxide or hydrosulfide ion as nucleophile was studied by Helling and Hendrickson [11], and in this work, deprotonation in the basic medium led directly to the formation of the CpFe complex of cyclohexadienone or cyclohexadienethione. In our laboratory, we have carried out nucleophilic substitution reactions with CpFe complexes of chlorobenzene and *o*-, *m*- or *p*-chlorotoluene with a number of amines as nucleophiles [12]. We have also reported that substitution reactions of the CpFe complex of *o*-dichlorobenzene with two nucleophilic groups located in the 1,2-positions of another benzene ring gave the CpFe complex of heterocyclic systems related to 9,10-dihydroanthracene with two heteroatoms at the 9,10-positions, and upon demetallation by pyrolytic sublimation, the free heterocyclic compounds were obtained [13]. More recently, we have shown that CpFe complexes of nitroarenes, as those of chloroarenes, could also undergo nucleophilic aromatic substitutions (S_NAr reactions) with a variety of nucleophiles [14,15], and further studies on mono- and disubstitutions with the CpFe complex of *o*-dichlorobenzene have been carried out [16]. Very similar studies have also been reported by a former colleague, U.S. Gill, in his post-doctoral work with Professor R.M. Moriarty [17–19].

As in the synthesis of heterocyclic systems reported earlier [13], the S_NAr reactions with the CpFe complexes have potentials for synthetic applications since demetallation of the S_NAr reaction products could lead to the formation of substituted arenes that may otherwise be difficult to obtain. Recently, we have reported on the successful synthesis of a number of arylated diethyl malonates via the S_NAr reaction between various CpFe complexed chloroarenes and the diethyl malonate anion, followed by the pyrolytic sublimation of the reaction product [20]. In the present work, S_NAr reactions were carried out with a number of CpFe complexes including the CpFe complex of 2,6-dimethylchlorobenzene or 2,6-dimethylnitrobenzene in order to study possible effects of steric hindrance, and the CpFe complexes of *m*-dichlorobenzene and *p*-dichlorobenzene in order to obtain data for comparison with those previously reported for the CpFe complex of *o*-dichlorobenzene [16]. Demetallation by pyrolytic sublimation on some of the S_NAr products was also investigated as a method of synthesis for a number of substituted arenes.

Results and discussion

In S_NAr reactions with CpFe complexes of chloroarenes or nitroarenes, the formation of a C–C bond in reactions with carbanion nucleophiles, such as those derived from diethyl malonate (DEM) and ethyl acetoacetate (EAA), could be potentially among the most useful for synthetic applications [15–17]. In our recent synthesis of arylated diethyl malonates [20], one of the compounds prepared was diethyl *p*-tolylmalonate (IIIa) obtained from pyrolytic sublimation of S_NAr product IIa from the reaction between η^6 -*p*-chlorotoluene- η^5 -cyclopentadienyliron hexafluorophosphate (I) with DEM/ K_2CO_3 . In the present work, reaction of I with the carbanion derived from EAA gave the expected S_NAr product, η^6 -ethyl α -(*p*-tolyl)acetoacetate- η^5 -cyclopentadienyliron hexafluorophosphate (IIb). However, attempted demetallation of IIb by pyrolytic sublimation [13,21] or photolysis [21] led to decomposition without the isolation of any pure product, although signals attributable to ethyl α -*p*-tolylacetoacetate (IIIb) could be identified in the 1H NMR spectrum of the mixture of products from the demetallation. In another experiment, reaction of I with α -benzoylacetophenone (dibenzoylmethane, DBM) in the presence of K_2CO_3 in THF/DMSO also gave the expected S_NAr products, η^6 -dibenzoyl-*p*-tolylmethane- η^5 -cyclopentadienyliron hexafluorophosphate (IIc), which, upon pyrolytic sublimation, gave rise to dibenzoyl-*p*-tolylmethane (IIIc), a compound that has not been reported previously. Shown in Scheme 1 are the transformations described above starting from the *p*-chlorotoluene complex I as substrate.

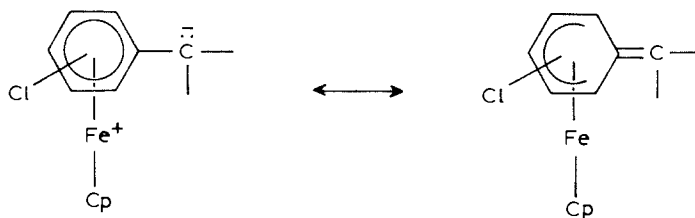
Also shown in Scheme 1 are the results from our earlier study with the CpFe complex of *o*-dichlorobenzene (IV) [16]. Reaction of IV with the carbanion nucleophile derived from DEM, EAA or DBM was found to give only monosubstitution products Va, Vb or Vc, respectively, while a similar reaction of IV with acetylacetone (diacetylmethane, DAM)/ K_2CO_3 resulted in deacetylation, giving rise to monosubstitution product Vd [16,17]. In the synthesis of arylated diethyl malonates [20], monosubstitution was also observed in the reaction of the CpFe complex of *m*- or *p*-dichlorobenzene (VII or X, respectively) with DEM/ K_2CO_3 to



Scheme 1

give VIIIa or XIa, and demetallation of Va, VIIIa and XIa, respectively, gave diethyl *o*-, *m*- and *p*-chlorophenylmalonates (VIa, IXa and XIIa, respectively). In the present work, S_NAr reactions between *m*-dichlorobenzene complex VII or *p*-dichlorobenzene complex X with carbanion nucleophiles from EAA, DBM and DAM were carried out, thus completing all the reactions between the CpFe complexes of *o*-, *m*- and *p*-dichlorobenzenes with DME, EAA, DBM and DAM.

Similar to the behavior of *o*-dichlorobenzene complex IV, reaction of VII or X with EAA, DBM or DAM in the presence of K_2CO_3 resulted in monosubstitution, as shown in Scheme 1, giving rise to S_NAr products VIIIb, VIIIc or VIII d from VII, and XIb, XIc or XI d from X, VIII d and XI d again being the result of deacetylation in the reactions with DAM. As suggested previously [16], the lack of formation of any disubstitution products in these S_NAr reactions with the various carbanion nucleophiles probably could be attributed to deprotonation of the S_NAr product in the basic reaction medium to give a zwitterion-cyclohexadienyl complex XIII, which would be more electron-rich than the original *o*-, *m*- or *p*-dichlorobenzene complex, thus rendering the second chloro group unreactive towards further nucleophilic substitution.



(XIII)

Attempts were carried out on the demetallation of the S_NAr products from VII and X obtained in the present work and those prepared previously [16] from the *o*-dichlorobenzene complex IV. Similar to the behavior of IIb from the reaction of I with EAA, pyrolytic sublimation or photolysis of Vb, VIIIb or XIb, the S_NAr product from reaction of the *o*-, *m*- or *p*-dichlorobenzene complex with EAA, led to decomposition with no isolable pure product. However, from the 1H NMR spectrum of each crude product mixture, signals attributable to the demetallated ethyl α -(*o*-, *m*- or *p*-chlorophenyl)acetoacetate (VIb, IXb, or XIIb, respectively) could be identified, and these signals indicated that VIb, IXb or XIIb was present to the extent of roughly 1/3 of the product mixture. Pyrolytic sublimation of Vc, VIIIc and XIc, from reactions with the carbanion of DBM as nucleophile, proceeded without difficulty to give *o*-, *m*- and *p*-chlorophenyl substituted dibenzoylmethane (VIc, IXc and XIc, respectively) as compounds that have not been reported previously. Similarly, pyrolytic sublimation of S_NAr products Vd, VIII d and IX d from reactions of IV, VII and X with DAM also proceeded without difficulty, but the demetallated products, *o*-, *m*- and *p*-chlorophenylacetone (VI d, IX d and XI d, respectively) are known compounds [22–24]. The yields and spectral data for the various S_NAr products from complex I, VII or X as substrate and for the substituted arenes obtained in the demetallation studies are summarized in Tables 1 to 4.

In previous work on S_NAr reactions with CpFe complexed chloroarenes and

Table 1
Yields and ^1H NMR data for the $\text{S}_{\text{N}}\text{Ar}$ products from reactions with I, VII and X ^a

Product ^b	Yield (%)	δ (ppm from TMS)			Others
		Solvent	Cp	Complexed Ar	
IIb, $p\text{-CH}_3\text{C}_6\text{H}_4\text{-CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5\text{)FeCp}^+$	70	CD_3CN	5.20(s,5H)	6.50(br.s,4H)	1.40(t,3H,CH ₃); 2.33(s,3H,CH ₃ ,CO); 2.60(s,3H,CH ₃ ,Ph); 4.45(q,2H,CH ₂); 5.18(s,1H,OH)
IIc, $p\text{-CH}_3\text{C}_6\text{H}_4\text{-CH}(\text{COC}_2\text{H}_5)_2\text{)FeCp}^+$	70	CD_3CN	4.80(s,5H)	6.30–6.95(m,4H)	2.50(s,3H,CH ₃ ,Ph); 7.23(s,1H,CH) 7.36–7.70(m,6H,Ph); 7.90–8.20(m,4H,Ph)
VIIIb, $m\text{-ClC}_6\text{H}_4\text{-CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5\text{)FeCp}^+$	75	$(\text{CD}_3)_2\text{CO}$	5.26(s,5H)	6.50–6.95(m,4H)	1.38(t,3H,CH ₃); 2.44(s,3H,CH ₃ ,CO); 4.38(q,2H,CH ₂); 5.40(s,1H,OH)
VIIIc, $m\text{-ClC}_6\text{H}_4\text{-CH}(\text{COC}_2\text{H}_5)_2\text{)FeCp}^+$	68	CD_3CN	4.83(s,5H)	6.36–6.95(m,4H)	7.00(s,1H,OH); 7.53–7.86(m,6H,Ph); 8.03–8.30(m,4H,Ph)
VIIIId, $m\text{-ClC}_6\text{H}_4\text{-CH}_2\text{COCH}_3\text{)FeCp}^+$	75	$(\text{CD}_3)_2\text{CO}$	5.16(s,5H)	6.03–6.76(m,4H)	2.30(s,3H,CH ₃); 4.10(s,2H,CH ₂)
XIb, $p\text{-ClC}_6\text{H}_4\text{-CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5\text{)FeCp}^+$	81	$(\text{CD}_3)_2\text{CO}$	5.27(s,5H)	6.59–6.63(m,2H) 6.89–6.91(m,2H)	1.39(t,3H,CH ₃); 2.24(s,3H,CH ₃ ,CO); 4.42(q,2H,CH ₂); 5.38(s,1H,OH)
XIc, $p\text{-ClC}_6\text{H}_4\text{-CH}(\text{COC}_2\text{H}_5)_2\text{)FeCp}^+$	70	CD_3CN	4.80(s,4H)	6.60(br.s,4H)	6.93(s,1H,OH); 7.35–7.90(m,6H,Ph); 8.03–8.40(m,4H,Ph)
XId, $p\text{-ClC}_6\text{H}_4\text{-CH}_2\text{COCH}_3\text{)FeCp}^+$	63	$(\text{CD}_3)_2\text{CO}$	5.23(s,5H)	6.16–7.43(m,2H) 6.53–6.80(m,2H)	2.30(s,3H,CH ₃); 4.10(s,2H,CH ₂)

^a I, VII and X are the hexafluorophosphates of $\eta^6\text{-}p\text{-chlorotoluene-}\eta^5\text{-cyclopentadienyliron}$, $\eta^6\text{-}m\text{-dichlorobenzene-}\eta^5\text{-cyclopentadienyliron}$ and $\eta^6\text{-}p\text{-dichlorobenzene-}\eta^5\text{-cyclopentadienyliron}$ cations, respectively. ^b The cations shown were obtained as their hexafluorophosphates, IIb and IIc, VIIIb, VIIIc and VIIIId, and XIb, XIc and XIId, being derived from reactions with I, VII, and X, respectively; satisfactory C and H analyses were obtained for all of these products.

Table 2

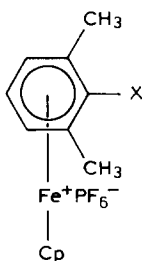
IR carbonyl absorptions and ^{13}C NMR data for the $S_{\text{N}}\text{Ar}$ products from reactions with I, VII, and X

Product	$\nu(\text{CO})$ (cm^{-1})	$\delta(\text{CD}_3\text{CN})$ (ppm from TMS) ^a		
		Cp	Complexed Ar	Others
IIb	1725	78.4	87.6, 88.7, 89.2, 89.3	14.1(CH_3CH_2); 20.3(CH_3Ph); 29.5(CH_3CO); 62.5(CH); 63.4(CH_2); 167.3(COOEt); 199.5(CH_3CO)
	1740			
IIc	1690	78.2	88.7, 89.1, 98.9*, 104.4*	58.4(CH); 130.0, 130.6, 135.9, 136.1*(Ph); 192.9(CO)
	1705			
VIIIb	1715	78.7	86.4, 86.7, 86.8, 88.5 97.9*, 106.0*	12.3(CH_3CH_2); 28.1(CH_3CO); 60.5(CH); 62.2(CH_2); 165.1(COOEt); 197.7(CH_3CO)
	1730			
VIIIc	1680	78.9	86.9, 87.5, 87.6, 88.9 99.4*, 106.4*	56.8(CH); 128.6, 129.1, 134.5, 134.8*(Ph); 190.9(CO)
	1700			
VIIId ^b	1710	79.0	87.3, 87.3, 88.2, 89.6 100.3*, 106.4*	29.7(CH_3); 47.0(CH_2); 203.9(CO)
XIb	1715	79.3	87.0, 87.6, 87.9, 88.4 97.4*, 106.4*	12.8(CH_3CH_2); 28.6(CH_3CO); 60.8(CH); 62.7(CH_2); 165.8(COOEt); 198.3(CH_3CO)
	1735			
XIc	1680	79.0	87.5, 88.3, 98.6* 106.4*	56.6(CH); 128.5, 129.1, 134.4, 134.5*(Ph); 190.9(CO)
	1700			
XIId ^b	1715	79.1	88.0, 89.0, 99.4*, 105.8*	29.7(CH_3); 46.8(CH_2); 203.9(CO)

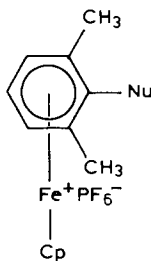
^a Asterisks denote quaternary carbons. ^b The solvent for the NMR study was $(\text{CD}_3)_2\text{SO}$ instead of CD_3CN .

nitroarenes, various N-, O- and S-containing functions, besides carbanions, have been utilized as nucleophiles. In order to investigate the possibility of steric hindrance in such reactions, the CpFe complex of 2,6-dimethylchlorobenzene (XIVa) or 2,6-dimethylnitrobenzene (XIVb) was employed as substrate in a number of $S_{\text{N}}\text{Ar}$ reactions. The nucleophilic groups employed were derived from NH_3 , $(\text{CH}_3)_2\text{NH}$, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{NH}_2$, pyrrolidine ($\text{C}_4\text{H}_8\text{NH}$), $\text{CH}_3\text{CH}_2\text{OH}$, $\text{C}_6\text{H}_5\text{OH}$, *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{SH}$, $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$ (EAA), and $\text{CH}_2(\text{COC}_6\text{H}_5)_2$ (DBM). The $S_{\text{N}}\text{Ar}$ products obtained were XVa to XVh, with $\text{Nu} = \text{NH}_2$, $(\text{CH}_3)_2\text{NH}$, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{NH}$, $\text{C}_4\text{H}_8\text{N}$ (*N*-pyrrolidinyl), $\text{CH}_3\text{CH}_2\text{O}$, $\text{C}_6\text{H}_5\text{O}$, *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{S}$, and $\text{CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5$, respectively. For each of these products, similar yields were obtained from the reaction with either XIVa or XIVb, and there was no significant effect of steric hindrance in the formation of XVa to XVh. It may be noted that in previous studies, *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SH}$ has been used as a source of a S-nucleophile [14,16]. In the present work, *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{SH}$ was employed in order to enhance the possibility of steric hindrance, but $S_{\text{N}}\text{Ar}$ product XVg was formed in the reaction of XIVa or XIVb with *o*-thiocresol without significant steric effects. In the attempted reaction of XIVa or XIVb with DBM, however, no $S_{\text{N}}\text{Ar}$ product was observed, suggesting that only with the very bulky nucleophile derived from DBM was steric hindrance sufficiently large to account for the lack of $S_{\text{N}}\text{Ar}$ reaction with substrate XIVa or XIVb, in which both *o*-positions to the leaving group were also hindered by CH_3 substituents.

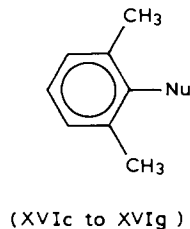
It has been reported that pyrolytic sublimation of the $S_{\text{N}}\text{Ar}$ product from reaction of XIVa with the carbanion derived from DEM gave rise to diethyl 2,6-dimethylphenylmalonate [20]. Of the $S_{\text{N}}\text{Ar}$ products XVa to XVh, XVa, ob-



(XIVa, X = Cl ;
XIVb, X = NO₂)



(XVa to XVh)



Designation as a to h, respectively,
for Nu = NH₂, (CH₃)₂NH, CH₃(CH₂)₃NH,
C₄H₈N (*N*-pyrrolidiny), CH₃CH₂O,
C₆H₅O, *o*-CH₃C₆H₄S, and CH(COCH₃)COOC₂H₅

tained in yields of 56 and 59%, respectively, from reactions of XIVa and XIVb with NH₃, is a known compound [25] and its demetallation by pyrolytic sublimation gave a 60% yield of the commercially available 2,6-dimethylaniline. Complexes XVb and XVh, obtained from reaction of XIVa or XIVb with (CH₃)₂NH and EAA, respectively, decomposed upon heating during the attempted demetallation. On the other hand, pyrolytic sublimation of XVC to XVg gave the corresponding demetallated substituted arenes XVIc to XVIg, only two of which, XVIc [26] and XVIe [27], have been reported previously. The new compounds obtained, *N*-butyl-2,6-dimethylaniline (XVIc), 2,6-dimethylethoxybenzene (XVIe) and 2,6-dimethyl-*o*-tolylthio-benzene (XVIg), together with new compounds IIIc, VIc, IXc and XIIc described earlier, thus further demonstrate that S_NAr reactions with CpFe complexes followed by demetallation could be a useful method for the synthesis of certain substituted arenes. The yields and spectral data for S_NAr products XIb to XVh, and demetallation products XVIc to XVIg, are summarized in Tables 5–8.

Experimental

Preparation of substrates

The CpFe complexes of *p*-chlorotoluene (I), and *o*-, *m*- and *p*-dichlorobenzenes (IV, VII and X, respectively) were prepared by ligand exchange reactions as reported by Khand, Pauson and Watts [28]. Similarly, ligand exchange also gave the CpFe complex of 2,6-dimethylchlorobenzene (XIVa) [20]. The CpFe complex of 2,6-dimethylnitrobenzene (XIVb) was obtained from the corresponding 2,6-dimethylaniline complex by oxidation with H₂O₂ in CF₃COOH [25].

Reactions with carbanion nucleophiles

A mixture of 1.0 mmol of I, VII, or X, 1.1 mmol of ethyl acetoacetate (EAA), dibenzoylmethane (DBM) or diacetylmethane (DAM), and 2.5 mmol of K₂CO₃ in 10 ml of a 1/1 mixture of THF/DMSO was stirred at room temperature and under N₂ for 5 h. The resulting material was filtered into 10 ml of a 10% HCl solution.

Table 3

Yields and ^1H NMR data for substituted arenes from demetallation of $\text{S}_{\text{N}}\text{Ar}$ products from reactions with I, IV, VII and X

Substituted arene ^a	Yield (%)	δ (acetone- <i>d</i> ₆) (ppm from TMS)
IIIb, <i>p</i> -CH ₃ C ₆ H ₄ CH-(COCH ₃)COOC ₂ H ₅ ^b	–	1.21(t,3H,CH ₃); 2.34(s,3H,CH ₃ CO); 4.28(q,2H,CH ₂); 4.62(s,1H,CH); 7.20–7.42(m,Ar)
IIIc, <i>p</i> -CH ₃ C ₆ H ₄ CH-(COC ₆ H ₅) ₂	70	2.24(s,3H,CH ₃); 6.54(s,1H,CH); 7.07–7.17(m,3H), 7.21–7.28(m,3H), 7.37–7.53(m,5H), 7.96–8.00(m,3H)(Ar)
VIb, <i>o</i> -ClC ₆ H ₄ CH(C-OCH ₃)COOC ₂ H ₅ ^b	–	1.27(t,3H,CH ₃); 2.23(s,3H,CH ₃ CO); 4.21(q,2H,CH ₂); 5.33(s,1H,CH); 7.16–7.40(m,Ar)
VIc, <i>o</i> -ClC ₆ H ₄ CH-(COC ₆ H ₅) ₂	79	7.14–7.55(m,10H), 7.97–8.06(m,4H)(Ar), CH,1H, hidden under Ar
VIId, <i>o</i> -ClC ₆ H ₄ CH ₂ -COCH ₃ ^c	88	2.21(s,3H,CH ₃); 3.85(s,2H,CH ₂); 7.12–7.30(m,3H), 7.35–7.48(m,1H)(Ar)
IXb, <i>m</i> -ClC ₆ H ₄ CH(CO-CH ₃)COOC ₂ H ₅ ^b	–	1.30(t,3H,CH ₃); 2.24(s,3H,CH ₃ CO); 4.30(q,2H,CH ₂); 4.72(s,1H,CH); 7.20–7.40(m,Ar)
IXc, <i>m</i> -ClC ₆ H ₄ CH-(COC ₆ H ₅) ₂	83	7.25(s,1H,CH); 7.12–7.18(m,1H), 7.21–7.29(m,3H), 7.45–7.60(m,7H), 7.96–8.01(m,3H)(Ar)
IXd, <i>m</i> -ClC ₆ H ₄ CH ₂ -COCH ₃ ^c	75	2.18(s,3H,CH ₃); 3.68(s,2H,CH ₂), 7.11–7.36(m,4H,Ar)
XIIb, <i>p</i> -ClC ₆ H ₄ CH(CO-CH ₃)COOC ₂ H ₅ ^b	–	1.24(t,3H,CH ₃); 2.32(s,3H,CH ₃ CO); 4.28(q,2H,CH ₂); 4.62(s,1H,CH); 7.20–7.42(m,4H,Ar)
XIIc, <i>p</i> -ClC ₆ H ₄ CH-(COC ₆ H ₅) ₂	76	6.55(s,1H,CH); 7.42–7.62(m,10H), 7.91–8.01(m,4H)(Ar)
XIIId, <i>p</i> -ClC ₆ H ₄ CH ₂ -COCH ₃ ^c	73	2.17(s,3H,CH ₃); 3.67(s,2H,CH ₂), 7.12, 7.30(two d,4H,Ar)

^a Satisfactory C and H analyses and correct molecular weights from the molecular ions in the mass spectra were obtained for these compounds except IIIb, VIb, IXb and XIIb. ^b IIIb, VIb, IXb and XIIb could not be isolated because of decomposition during demetallation; the ^1H NMR data were deduced from the spectra of the product mixtures obtained on demetallation. ^c These compounds have been reported in Ref. 14–16.

The reaction flask was washed with CH_2Cl_2 and the washing also filtered into the 10% HCl. A solution of 1.0 mmol of NH_4PF_6 in 20 ml of H_2O was then added and the product was recovered by extraction with a 4/1 mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{NO}_2$ (3×25 ml). The combined extracts was washed with H_2O (5×25 ml), dried over MgSO_4 , and the solvent removed by a rotary evaporator. The residual material was washed with ether and the product was crystallized or precipitated in CH_2Cl_2 /ether to give IIb,c, VIIIb,c or XIb,c, from I, VII or X, respectively.

In the reactions with DAM, the above treatment gave an impure product. The procedure was slightly modified by allowing the filtered reaction mixture in the 10% HCl solution to stir at room temperature for 1 h before the NH_4PF_6 was introduced. In this way the pure deacetylated product VIIIId or XIId was obtained from VIII or X, respectively.

Table 4

IR carbonyl absorptions and ^{13}C NMR data for substituted arenes from demetallation of $\text{S}_{\text{N}}\text{Ar}$ products from reactions with I, IV, VII and X

Substituted arene	$\nu(\text{CO})$ (cm^{-1})	$\delta(\text{Acetone-}d_6)(\text{ppm from TMS})^a$
IIIc	1675 1698	62.1(CH); 128.3, 128.4(2C), 128.5(4C), 128.6(4C), 129.1, 129.4, 132.2*, 133.2, 135.6*(2C), 137.4*(Ar); 194.0(2C)(CO)
VIc	1678 1700	58.7(CH); 127.1, 128.3*, 128.6(4C), 128.9(4C), 129.4, 129.7(2C), 131.4*(2C), 131.5, 133.6, 135.6*(Ar); 193.8(2C)(CO)
VIId	1710	29.5(CH ₃); 48.2(CH ₂); 126.9, 128.6, 129.4, 131.5, 134.3*, 136.5*(Ar); 204.8(CO)
IXc	1690 1720	44.8(CH); 127.1, 127.7, 128.5(4C), 128.7(4C), 129.6, 129.8(2C), 133.4, 134.3*, 136.3*, 136.4*(2C)(Ar); 196.8(2C)(CO)
IXd	1710	29.4(CH ₃); 50.2(CH ₂); 127.2, 127.6, 129.5, 129.9, 134.3*, 135.9*(Ar); 205.4(CO)
XIIc	1675 1695	44.4(CH); 128.1, 128.6(4C), 128.8(4C), 128.9(2C), 130.8(2C), 131.2(2C), 133.9*(2C), 135.4*, 136.2*(Ar); 193.6(2C)(CO)
XIIId	1715	29.3(CH ₃); 49.9(CH ₂); 128.8(2C), 130.7(2C), 132.5*, 132.9*(Ar); 205.5(CO)

^a Asterisks denote quaternary carbons.

For the reaction of XIVA or XIVb with EAA or DBM, the same procedure was employed except that, instead of stirring at room temperature, the reaction mixture was heated under reflux and under N_2 for 5 h. The product from reaction of XIVA or XIVb with EAA was XVh, while no reaction was observed from the treatment of XIVA or XIVb with DBM.

Reactions with *N*-containing nucleophiles

A mixture of 1.0 mmol of XIVA or XIVb and 5.0 mmol of *n*-butylamine or pyrrolidine in 10 ml of a 1/1 mixture of THF/DMSO was heated under reflux and under N_2 for 2 h. A solution of 1.0 mmol of NH_4PF_6 in 20 ml of H_2O was added and the product was recovered by extraction with CH_2Cl_2 (3×25 ml). The combined extract was treated as described above for reactions with carbanion nucleophiles to give XVC or XVD, respectively, from reaction with *n*-butylamine or pyrrolidine.

In similar reactions with NH_3 or $(\text{CH}_3)_2\text{NH}$, 1.0 mmol of XIVA or XIVb in 10 ml of THF/DMSO was heated under reflux and under N_2 , and gaseous NH_3 or $(\text{CH}_3)_2\text{NH}$ was passed into the reaction mixture for 2 h. The resulting material was stirred at room temperature for an additional 3 h and then worked up as in the reaction with *n*-butylamine or pyrrolidine to give XVA or XVB, respectively, from reaction with NH_3 or $(\text{CH}_3)_2\text{NH}$.

Reactions with *O*- or *S*-containing nucleophiles

A mixture of 1.0 mmol of XIVA or XIVb, 1.1 mmol of phenol or 2.0 mmol of *o*-thiocresol, and 2.5 mmol of K_2CO_3 in 10 ml of THF/DMSO was heated under reflux and under N_2 for 5 h. The resulting material was filtered into a 10% HCl solution and worked up as described in the reactions with carbanion nucleophiles to

Table 5
Yields and ^1H NMR data for the $S_N\text{Ar}$ products from reactions with XIVa and XIVb^a

Product ^b	Yield (%) ^c		$\delta(\text{CD}_3\text{CN})$ (ppm from TMS)			
	A	B	Cp	Complexed Ar	Others	
XVb, 2,6-(CH_3) ₂ C_6H_3 - ($\text{N}(\text{CH}_3)_2$) FeCp^+	51	57	4.86(s,5H)	5.91(t,1H) 6.03(d,2H)	2.97(s,6H, CH_3 ,N); 2.40(s,6H, CH_3 ,Ph)	
XVc, 2,6-(CH_3) ₂ C_6H_3 (NHCH_2 - (CH_2) ₂ CH_3) FeCp^+	68	69	4.70(s,5H)	5.69(t,1H) 5.90(d,2H)	0.93(t,3H, CH_3); 1.37(sextet,2H, γ - CH_2); 1.56(quintet,2H, β - CH_2); 2.36(s,6H, CH_3 ,Ph); 3.26(A Bq,2H, α - CH_2); 4.02(br.s,1H,NH)	
XVd, 2,6-(CH_3) ₂ C_6H_3 - (NC_4H_8) FeCp^+ ^d	70	65	4.87(s,5H)	5.92(t,1H) 6.05(d,2H)	2.04(br.s,4H, $\text{C}_4\text{H}_2\text{CH}_2$); 2.39(s,6H, CH_3 ,Ph); 3.36(br.s,4H, $\text{C}_4\text{H}_2\text{N}$)	
XVe, 2,6-(CH_3) ₂ C_6H_3 - (OC_2H_5) FeCp^+	82	78	4.83(s,5H)	5.87(t,1H) 6.08(d,2H)	1.40(t,3H, CH_3); 2.46(s,6H, CH_3 ,Ph); 3.91(q,2H, CH_2)	
XVf, 2,6-(CH_3) ₂ C_6H_3 - (OC_6H_5) FeCp^+	69	65	4.98(s,5H)	6.04(t,1H) 6.20(d,2H)	2.32(s,6H, CH_3 ,Ph); 6.83(d,2H), 7.12(t,1H)7.34(t,2H)(C_6H_5)	
XVg, 2,6-(CH_3) ₂ C_6H_3 - ($\text{SC}_6\text{H}_4\text{CH}_3$ -o) FeCp^+	78	63	4.97(s,5H)	6.22(t,1H) 6.30(d,2H)	2.45(s,3H, CH_3 ,Ph); 2.51(s,6H, CH_3 ,Ph); 6.57(d,1H), 7.01(6.1H), 7.14(t,1H), 7.26(d,1H)(C_6H_4)	
XVh, 2,6-(CH_3) ₂ C_6H_3 ($\text{CH}(\text{CO}-$ CH_3) COOC_2H_5) FeCp^+	68	65	4.92(s,5H)	6.16(t,1H) 6.28(d,2H)	1.38(s,3H, CH_3 ,CO); 1.45(t,3H, C_2H_5 , CH_2); 2.27(s,6H, CH_3 ,Ph); 4.54(q,2H, CH_2); 7.37(s,1H,CH)	

^a XIVa and XIVb are the hexafluorophosphates of η^6 -2,6-dimethylchlorobenzene- η^5 -cyclopentadienyliron and η^6 -2,6-dimethylnitrobenzene- η^5 -cyclopentadienyliron cations, respectively. ^b The cations shown were obtained as their hexafluorophosphates; satisfactory C and H analyses were obtained for all of these compounds. ^c A and B designate yields from reactions with XIVa and XIVb, respectively. ^d $\text{NC}_4\text{H}_8 = N$ -pyrrolidinyli.

Table 6

IR and ^{13}C NMR data for the $S_N\text{Ar}$ products from reactions with XIVa and XIVb

Product	IR (cm^{-1})	δ (CD_3CN)(ppm from TMS) ^a		
		Cp	Complexed Ar	Others
XVb	–	77.4	84.8(C4), 89.0(C3,5), 100.1*(C2,6), 125.0*(C1)	19.8(CH_3Ph); 44.2(CH_3N)
XVc	3405(NH)	77.6	82.1(C4), 88.4*(C2,6), 88.7(C3,5), 126.1*(C1)	14.2(CH_3); 20.0(CH_3Ph); 20.7($\gamma\text{-CH}_2$); 33.8($\beta\text{-CH}_2$); 48.1($\alpha\text{-CH}_2$)
XVd	–	77.4	84.9(C4), 89.1(C3,5), 101.1*(C2,6), 120.4*(C1)	19.8(CH_3Ph); 27.2(CH_2CH_2); 52.7(CH_2N)
XVe	–	78.6	85.4(C4), 88.4(C3,5), 98.8*(C2,6), 131.1*(C1)	15.8(CH_3), 16.9(CH_3Ph); 71.6(CH_2)
XVf	–	79.3	86.4(C4), 88.7(C3,5), 99.6*(C2,6), 126.5* C(1)	16.7(CH_3Ph); 115.9(2C), 124.5(1C), 131.3(2C), 157.7*(1C)(Ph)
XVg	–	79.5	88.0(C4), 89.6(C3,5), 100.7*(C1), 108.2*(C2,6)	20.2(CH_3); 21.3(2,6- CH_3); 127.2, 127.8, 128.1, 131.6, 134.6*, 137.3*(Ph)
XVh	1640, 1720(CO)	78.8	87.3(C4), 88.0(C3,5), 96.7* C(1), 103.7*(C2,6)	15.2(CH_3); 20.0(CH_3CO); 20.2(CH_3Ph); 63.1(CH_2); 105.5(CH); 171.2(COOEt); 179.7(CO)

^a Asterisks denote quaternary carbons.

give XVf or XVg. In the reaction with ethanol, a mixture of 1.0 mmol of XIVa or XIVb and 2.5 mmol of K_2CO_3 in 50 ml of ethanol was heated under reflux and under N_2 for 12 h and then worked up as above to give XVe.

Table 7

Yields and ^1H NMR data for substituted arenes from demetallation of $S_N\text{Ar}$ products from reactions with XIVa and XIVb

Substituted arene ^a	Yield (%)	δ (acetone- d_6)(ppm from TMS)
XVIc, 2,6-(CH_3) ₂ C_6H_3 - $\text{NH}(\text{CH}_2)_3\text{CH}_3$	78	0.92(t,3H, CH_3); 1.32–1.39(m,2H, $\gamma\text{-CH}_2$); 1.60–1.80(m, $\beta\text{-CH}_2$); 3.20–3.25(m,2H, $\alpha\text{-CH}_2$); 2.38(br.s,6H, CH_3Ph); 6.20(br.s,1H,NH); 7.06(br.s,3H,Ar)
XVId, 2,6-(CH_3) ₂ C_6H_3 - NC_4H_8 ^b	72	1.95–1.99(m,4H, CH_2); 2.25(s,6H, CH_3); 3.15–3.20(m,4H, CH_2N); 6.94(t,1H), 7.01(d,2H)(Ar)
XVIe, 2,6-(CH_3) ₂ C_6H_3 - OC_2H_5	75	1.41(t,3H, CH_3); 2.28(s,6H, CH_3Ph); 3.84(q,2H, CH_2); 6.90(t,1H), 7.00(d,2H)(Ar)
XVIIf, 2,6-(CH_3) ₂ C_6H_3 - OC_6H_5 ^c	75	2.12(s,6H, CH_3); 6.75(d,2H); 6.96(t,1H)(Ar); 7.02–7.13(m,3H), 7.24(t,2H)(Ar)
XVIg, 2,6-(CH_3) ₂ C_6H_3 - $\text{SC}_6\text{H}_4\text{CH}_3$ - ^d	74	2.39(s,6H, CH_3); 2.43(s,3H, CH_3); 6.39(d,1H), 6.89–6.99(m,2H), 7.11–7.25(m,4H)(Ar)

^a Satisfactory C, H and N analyses and correct molecular weights from the molecular ions in the mass spectra were obtained for these compounds. ^b NC_4H_8 = *N*-pyrrolidinyl, compound previously reported in Ref. 18. ^c Compound previously reported in Ref. 19. ^d The solvent for the NMR study was CD_3CN instead of acetone- d_6 .

Table 8

IR and ^{13}C NMR data for substituted arenes from demetallation of $\text{S}_{\text{N}}\text{Ar}$ products from reactions with XIVa and XIVb

Substituted arene	IR (cm^{-1})	$\delta(\text{acetone-}d_6)$ (ppm from TMS) ^a
XVIc	3420(NH)	13.6(CH ₃); 19.4(γ -CH ₂); 19.9(2C,CH ₃ Ph); 33.0(β -CH ₂); 47.5(α -CH ₂); 126.4, 129.7(2C), 130.5*(2C), 137.9*(Ar)
XVID	–	17.6(2C,CH ₃); 26.5(2C,CH ₂); 50.0(2C,CH ₂ N); 118.0, 126.9*(2C), 128.5(2C), 138.4*(Ar)
XVIE	–	15.8(CH ₃); 16.2(2C,CH ₃ Ph); 67.8(CH ₂); 123.6, 128.7(2C), 130.9*(2C), 156.1*(Ar)
XVIF	–	16.3(2C,CH ₃); 114.6(2C), 121.2, 125.0, 128.9(2C), 129.6(2C), 131.5*(2C), 151.0*, 157.8*(Ar)
XVIG ^b	–	15.3(CH ₃); 21.7(2C,CH ₃); 124.1, 124.3, 126.4, 128.4(2C), 129.9(2C), 130.6*, 130.6*, 134.7*(2C), 137.0*, 143.9*(Ar)

^a Asterisks denote quaternary carbons. ^b The solvent for the NMR study was CD_3CN instead of acetone- d_6 .

Pyrolytic sublimation

A sample, usually 0.5–1.0 mmol, of an $\text{S}_{\text{N}}\text{Ar}$ reaction product was heated for 1.0 h at 200–220 °C and 1 torr in a Buchi-GKR-50 sublimator. The material that was collected on the cold finger was removed by dissolution with CHCl_3 . After the solvent was evaporated off from the CHCl_3 solution, the residue was purified by passage through a short column (about 5 cm) packed with F-20 alumina (Alcoa Chemical Co.), the product being eluted with a 1/1 mixture of $\text{CCl}_4/\text{CHCl}_3$. Removal of the solvent from the eluate gave the liberated substituted arene. The yields of various substituted arenes obtained in this way are given in Tables 3 and 7.

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