

Nucleophilic Addition of Cyclopentadienyliron Complex of Disubstituted Benzenes

Eun Mi Lee and Young Keun Chung*

Department of Chemistry, Seoul National University Seoul 151-742. Received June 25, 1990

The product distribution obtained by the addition of hydride of $^-CR_2CN$ ($R = H$ and Me) to (disubstituted benzene)- $FeCp^+$ is studied. The formation of the substituted arene from η^5 -cyclohexadienyl- η^5 -cyclopentadienyliron is described.

Introduction

The electrophilic activation of π -hydrocarbons by coordination to a transition metal moiety represents a fundamental process in organometallic chemistry.¹ Studies of nucleophilic addition to π -hydrocarbons activated in this manner have led to significant synthetic and mechanistic applications.²

For some years ago Watts³ showed that the reactivity of halobenzenes towards nucleophilic attack by methoxide ion in methanol increases through the series of π -attached residue: $Cr(CO)_3 < Mo(CO)_3 < FeCp^+ < Mn(CO)_3^+$. (Arene) $FeCp^+$ cations with various substituents can be made by treating ferrocene with the appropriate arene in the presence of $AlCl_3$ or indirect ways.⁴ Although (arene) $FeCp^+$ cations have more electrophilicity than (arene) chromium tricarbonyl complexes, (arene) $FeCp^+$ cations have been little studied with regard to their synthetic capability.⁵

Recently Sutherland and coworkers⁶ have studied the nucleophilic addition of hydride to fifteen $(C_6H_5X)FeCp^+$ cations with substituents X having different electron-donating or electron-withdrawing effects. They obtained m - and p -hydride addition products with $X = N,N$ -dimethyl, and o -addition product with $X = NO_2$. For the other 13 cations, o -, m - and p -hydride addition products were obtained in all cases, with a few instances also giving very minor amounts of ipso-adducts. They suggested that all kinds of factors including electronic, steric and free valency effects could exert their influence in giving rise to the overall results.

Watts and coworkers⁷ have studied the nucleophilic addition of methyllithium to a number of cyclopentadienyliron complexes of disubstituted arenes with arenes = o -, m -, p -xylene, o -, m -, p -dichlorobenzene, o -, m -, p -chlorotoluene, o -, m -, p -bromotoluene, and p -chloroanisole. The addition of methyllithium to (arene) $FeCp^+$ cations is subject in most cases to the same directive influences as for the hydride addition.⁷ The ortho-directing influence of a chlorine substituent was also found for the addition of methyllithium. The ortho and meta product ratio of ca. 4:1 observed for the p -chlorotoluene complex was the same (within experimental error) as that found for hydride addition. With aniline complex, the major product resulted from hydride addition to the m - and p -position, while in similar reactions with the nitrobenzene complex, the major product was derived from o -addition. These results were explained by the inductive and resonance effects of substituent X , influencing the charge distribution of the o -, m -, p -positions, and electron-donating substituents favoring nucleophilic addition at the meta-position, and electron-withdrawing substituents favoring o -addi-

tion.

In order to evaluate further the possible effects of various factors that may influence the site of hydride addition and the carbanion addition, we have examined the reaction of $NaBH_4$ and some carbonions with a series of (disubstituted-benzene) cyclopentadienyliron cations.

Experimental

All solvents were purified by standard methods and all synthetic procedures were done under a nitrogen atmosphere.

¹H-NMR spectra were measured on either Bruker AC80 or Varian XL-200. Infrared spectra were recorded on a Perkin-Elmer 782 spectrophotometer and mass spectra were recorded on a VG ZAB-E double focusing mass spectrometer.

η^6 -Disubstituted benzene- η^5 -cyclopentadienyliron Cations. Known methods were employed for the preparation of (disubstituted benzene) $FeCp^+$ cations, all of which were isolated as their hexafluorophosphate salts. o -, m -, p -Dichlorobenzene complexes, p -bromotoluene complex, and p -chloroanisole complex were prepared from ligand exchange reactions between ferrocene and arenes.^{4a} o -, m -, p -Dimethoxybenzene complexes were obtained via a nucleophilic substitution reaction between o -, m -, p -dichlorobenzene complexes and sodium methoxide in methanol solution.^{8,9} o -chloroanisole complex was obtained via a reaction between o -chlorophenol complex and diazomethane.⁹

Hydride Addition Reactions. As an illustration of the hydride addition reactions, a solution of 100 mg (0.247 mmol) of [(o -dimethoxybenzene) $FeCp$]PF₆ and 150 mg (4.0 mmol) of $NaBH_4$ in 30 ml of THF was filtered through a sintered glass filter, 15 ml of H₂O was added and the material was extracted with cyclohexane (3 × 25 ml). The combined extract was washed with H₂O, dried over MgSO₄, and the solvent was removed by a rotary evaporator. The residue was purified by passage through a short column (5 cm) packed with neutral alumina. The hydride addition products were eluted with diethyl ether. Upon removal of the solvent from the eluate, a 32% (21 mg) isolated yield of a mixture of 3A and 3B was obtained as red oil. The ratio of 3A and 3B was determined by ¹H-NMR to be 1:3.35.

3A. ¹H-NMR(CDCl₃) δ 5.80(d, $J = 5$, 1H³), 4.29(s, 5H, Cp), 4.05(m, 1H, H⁴), 3.77(s, 3H, OMe), 3.61(s, 3H, OMe), 2.39(m, 1H, H⁵), 3.03(dd, $J = 12.7$, 1H, H^{6-endo}), 1.85(d, $J = 12$, 1H, H^{6-exo}) ppm.

3B. ¹H-NMR(CDCl₃) δ 4.44(d, $J = 6.4$, 1H, H⁴), 4.29(s, 5H, Cp), 4.06(s, 3H, OMe), 3.37(s, 3H, OMe), 2.30(m, 1H, H^{6-endo}), 2.20(m, 1H, H⁵), 1.42(d, $J = 11.6$, 1H, H^{6-exo}) ppm.

Reaction between [(o -chloroanisole) $FeCp$]PF₆ and

NaBH₄. Under identical condition as above, a 12% isolated yield of 1-chlorocyclohexadienyl-cyclopentadienyliron compound was obtained. ¹H-NMR(CDCl₃) δ 5.94(t, J = 5, 1H, H³), 4.60(d, J = 5, 1H, H²), 4.36(s, 5H, Cp), 4.20(t, J = 5, 1H, H⁴), 2.90(dd, J = 12.6, 1H, H^{6-endo}), 2.60(t, J = 6, 1H, H⁵), 1.98(d, J = 12.6, 1H, H^{6-exo}) ppm; MS, *m/z*, 234 (M⁺), 198 (M⁺-H-Cl), 168 (M⁺-Cp-H), 112 (C₆H₅Cl).

Reaction between [(*p*-chloroanisole)FeCp]PF₆ and NaBH₄. Under identical condition as above, a 32% isolated yield of 1-chloro-4-methoxycyclohexadienyl-cyclopentadienyl-iron compound was obtained. ¹H-NMR(CDCl₃) δ 5.88(dd, J = 5.4, 2, 1H, H³), 4.54(dd, J = 5.4, 1.5, 1H, H⁴), 4.33(s, 5H, Cp), 2.82(m, 1H, H¹), 2.81(m, 1H, H^{6-endo}), 2.09(d, J = 11, 1H, H^{6-exo}) ppm; MS, *m/z*, 264(M⁺), 228(M⁺-H-Cl), 198(M⁺-OMe-Cl), 142(MeOC₆H₄Cl).

Preparation of Carbon Nucleophiles. Freshly prepared solutions of the carbon nucleophiles used in all experiments. The nucleophiles were generated as follows:

LiCMe₂CN. A solution of lithium diisopropylamide was prepared by dropwise addition *via* syringe of *n*-BuLi (1.2 ml of 2.5 M solution in hexane, 3.0 mmol) to diisopropylamine (0.4 ml, 3.0 mmol) in THF (15 ml) at -78°C. After 30 min, 2-methyl-propionitrile (0.27 ml, 3.0 mmol) was added dropwise. After being stirred for 30 min, the reagent solution was used in the addition reactions described below. The same procedure was used in the preparation of solution of LiCH₂CN.

General Procedure for Carbon Nucleophile Addition to (disubstituted benzene)FeCp⁺. To the suspension of [(disubstituted benzene)FeCp]PF₆ (1.5 mmol) in THF (30 ml) at -78°C was added carbon nucleophile (3.0 mmol) in 15 ml of THF. The reaction mixture was stirred for 1 h at -78°C. Then the reaction mixture was poured into water and extracted three times with diethyl ether (100 ml). The ether extract was dried over MgSO₄ and evaporated to dryness yielding the crude product as a orange-yellow solid.

Demetalation. The crude product in the above reaction was dissolved in cyclohexane. The resulting solution was stirred for 3 days at room temperature. After column chromatography on silica gel, mono-functionalized arene compound was obtained.

Reaction between [(*o*-dimethoxybenzene)FeCp]PF₆ and LiCH₂CN. Under identical condition as above, a 34% isolated yield of 4 was obtained. IR ν_{CN} 2250 cm⁻¹; ¹H NMR(CDCl₃) δ 6.85-6.82(m, 3H, arene), 3.89(s, 3H, OMe), 3.87(s, 3H, OMe), 3.70(s, 2H, CH₂) ppm; MS, *m/z*, 177(M⁺), 162(M⁺-Me).

Reaction between [(*m*-dimethoxybenzene)FeCp]PF₆ and LiCH₂CN. Under identical condition as above, a 34% isolated yield of a mixture of 5A and 5B, was obtained. The ratio of 5A and 5B was determined by ¹H NMR to be 3:2. IR ν_{CN} 2246 cm⁻¹; ¹H NMR(CDCl₃) δ 7.3-7.1(m, Ph), 6.7-6.4(m, Ph), 3.86(s, OMe, 5A), 3.83(s, OMe, 5B), 3.80(s, OMe, 5A), 3.79(s, OMe, 5B), 3.67(s, CH₂, 5A), 3.60(s, CH₂, 5B) ppm.

Reaction between [(*p*-dimethoxybenzene)FeCp]PF₆ and LiCH₂CN. Under identical condition as above, a 27% isolated yield of 6 was obtained. IR ν_{CN} 2250 cm⁻¹; ¹H NMR(CDCl₃) δ 6.95-6.81(m, arene ring protons), 3.81(OMe), 3.78(OMe), 3.67(CH₂) ppm.

Reaction between [(*o*-dimethoxybenzene)FeCp]PF₆ and LiMe₂CN. Under identical condition as above, a 60%

isolated yield of 7 was obtained. ¹H NMR(CDCl₃) δ 6.9-6.78(m, 3H, Ph), 3.87(s, 6H, OMe), 1.73(s, 6H, Me) ppm; ¹³C-NMR(CDCl₃) δ 149.28(C^{1,2}), 134.11(CN), 117.15, 111.45, 109.46(C^{3,5,6}), 56.0(OMe), 29.0(Me) ppm; IR ν_{CN} 2240 cm⁻¹; MS, *m/z*, 205(M⁺), 190(M⁺-Me), 175(M⁺-2Me), 149(M⁺-2Me-CN).

Reaction between [(*m*-dimethoxybenzene)FeCp]PF₆ and LiCMe₂CN. Under identical condition as above, a 51% isolated yield of a mixture of 8A and 8B was obtained. The ratio of 8A and 8B was determined by ¹H NMR to be 1:2. IR ν_{CN} 2230 cm⁻¹; ¹H NMR(CDCl₃) δ 6.82-6.36(m, Ph), 3.91(s, OMe, 8B), 3.88(s, OMe, 8A), 1.72(s, Me, 8B), 1.55(s, Me, 8A) ppm.

Reaction between [(*p*-dimethoxybenzene)FeCp]PF₆ and LiCMe₂CN. Under identical condition as above, a 55% isolated yield of 9, was obtained. IR ν_{CN} 2234 cm⁻¹; ¹H NMR(CDCl₃) δ 6.89-6.82(m, 3H, Ph), 3.84(s, 3H, OMe), 3.81(s, 3H, OMe), 1.64(s, 6H, Me) ppm.

Reaction between [(*p*-bromotoluene)FeCp]PF₆ and LiCMe₂CN. Under identical condition as above, a 59% isolated yield of 10 was obtained. The ortho addition to the methyl group was confirmed by analysis of ¹H NMR NOSEY spectrum of 7. IR ν_{CN} 2250 cm⁻¹; ¹H NMR(CDCl₃) δ 5.26(dd, J = 5.3, 1.7, 1H, H³), 4.60(dd, J = 5.3, 1.3, 1H, H²), 3.97(s, 5H, Cp), 2.87(dd, J = 6.9, 1.3, 1H, H⁶), 2.62(dd, J = 6.9, 1.7, 1H, H⁵), 1.44(s, 3H, Me), 0.76(d, J = 3.4, 6H, Me) ppm.

Reaction between [(*o*-dichlorobenzene)FeCp]PF₆ and LiCMe₂CN. Under identical condition as above, a 80% isolated yield of a mixture of 11A, and 11B was obtained. The isomer ratio of 11A and 11B was determined by ¹H NMR to be 3.1:1.

The mixture has the following properties: IR ν_{CN} 2230 cm⁻¹; MS, *m/z*, 335(M⁺), 300(M⁺-Cl), 267(M⁺-CMe₂CN).

11A. ¹H NMR(CDCl₃) δ 6.18(dd, J = 5, 1.2, 1H, H³), 4.4(m, 1H, H⁴), 4.42(s, 5H, Cp), 3.26(dd, J = 6.8, 0.7, 1H, H⁶), 2.96(m, 1H, H⁵), 0.96(d, J = 4, 6H, Me) ppm.

Reaction between [(*m*-dichlorobenzene)FeCp]PF₆ and LiCMe₂CN. Under identical condition as above, a 75% isolated yield of a mixture of 12A, 12B, and 12C, was obtained. The isomer ratio of 12A/12B/12C was determined by ¹H NMR to be 8.7:4.3:1.

The mixtures has the following properties: IR ν_{CN} 2232 cm⁻¹; MS, *m/z*, 335(M⁺), 300(M⁺-Cl), 267(M⁺-CMe₂CN).

12A. ¹H NMR(CDCl₃) δ 5.77(t, J = 5.2, 1H, H³), 4.73(dd, J = 5.2, 1.2, 2H, H^{2,4}), 3.62(t, J = 1.2, 1H, H⁶), 1.13(s, 6H, Me) ppm.

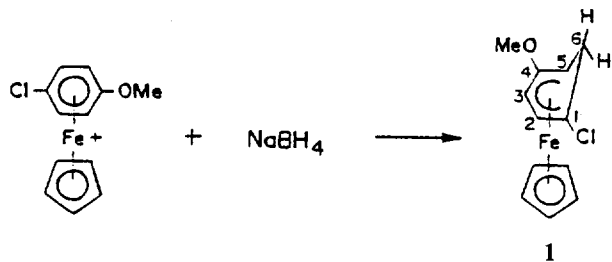
Reaction between [(*p*-dichlorobenzene)FeCp]PF₆ and LiCMe₂CN. Under identical condition as above, a 85% isolated yield of 13, was obtained. IR ν_{CN} 2228 cm⁻¹; ¹H NMR(CDCl₃) δ 6.08(dd, J = 5.3, 1.8, 1H, H³), 4.80(dd, J = 5.3, 1.6, 1H, H²), 3.41(dd, J = 6.9, 1.8, 1H, H⁵), 3.17(dd, J = 6.9, 1.6, 1H, H⁶), 0.98(s, 6H, Me) ppm.

Results and Discussion

Hydride Addition. Hydride addition reactions were carried out with disubstituted-benzene cyclopentadienyliron cations. The required cations were prepared from ferrocene by the ligand exchange procedure previously described^{4,7,9} and were purified by recrystallization of their hexafluorophosphate salt.

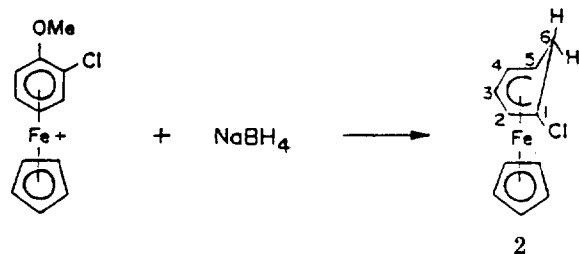
Upon treatment with NaBH_4 in THF, possible products could result from addition of the hydride ion to give cyclohexadienyl cyclopentadienyliron complexes. This addition proceeds from the site of the arene ring remote from the metal, leading to exo-added products. The structures assigned to these products were decided on the basis of their ^1H NMR spectra.

Reaction between $[(p\text{-chloroanisole})\text{FeCp}]\text{PF}_6$ and NaBH_4 gave 1-chloro-4-methoxycyclohexadienyl-cyclopentadienyliron, **1**. The meta directing effect of methoxy and the ortho



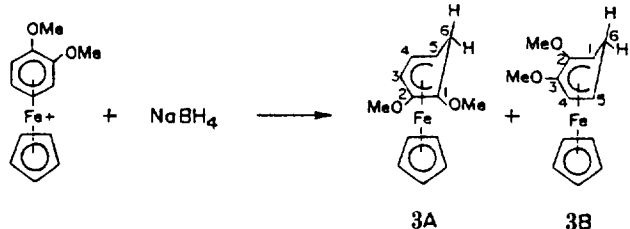
directing effect of chloride can reinforce to produce **1**. Puason⁸ studied the reaction between $[(m\text{-chloroanisole})\text{FeCp}]\text{PF}_6$ and NaBH_4 . They obtained the meta-addition to the methoxy as a major and the ortho-addition to the methoxy and chloro groups as a minor product. These results suggest that the directing effect of the methoxy group is more stronger than that of the chloro group.

Reaction between $[(o\text{-dichloroanisole})\text{FeCp}]\text{PF}_6$ and NaBH_4 gave 1-chlorocyclohexadienyl cyclopentadienyliron, **2**. The product was unexpected one. Nucleophilic substituent



tion of methoxy group in $[(o\text{-chloroanisole})\text{FeCp}]\text{PF}_6$ by hydride may proceed. Subsequently, the reaction of (chlorobenzene)-cyclopentadienyliron cation and an excess of NaBH_4 resulted in the *o*-adduct. The demethoxylation was rather rare. However, partial demethoxylation was reported in the addition of hydride to methoxy-substituted arene cyclopentadienyliron cations.⁸

Reaction between $[(o\text{-dimethoxybenzene})\text{FeCp}]\text{PF}_6$ and NaBH_4 resulted in the exo-addition of hydride ion to the C3(3A) and C4(3B) position in the ratio of 1:3.35. An estima-



tion of the relative proportions of **3A** and **3B** in the product

was determined by integration of the signals of the methoxy protons.

Reaction between $[(m\text{-dimethoxybenzene})\text{FeCp}]\text{PF}_6$ and NaBH_4 gave a mixture of 1,3-dimethoxycyclohexadienyl-cyclopentadienyliron, 2,4-dimethoxycyclohexadienyl-cyclopentadienyliron, and 1,5-dimethoxycyclohexadienyl-cyclopentadienyliron. The crude reaction mixture was continuously decomposed. Thus, we just confirmed the formation of three kind isomers. The relative ratio of three isomers was continuously changed. Finally, 2,4-dimethoxycyclohexadienyl-cyclopentadienyliron compound was left.

The reaction between $[(p\text{-dimethoxybenzene})\text{FeCp}]\text{PF}_6$ and NaBH_4 has been studied several years ago.⁸ There was only one product as we expected. The meta-directing influence of a methoxy substituent was found for the addition of hydride to the disubstituted benzene cyclopentadienyliron cations. For the $(\text{C}_6\text{H}_4\text{OMe-X})\text{FeCp}^+$ complex, a major factor may be the electron-donating resonance effect (+R), which would render the *m*-position the most electron deficient, thus giving rise to the *m*-adduct. However, the directive influence of methoxy group was not big enough one isomer to be predominant.

Thus, the directive effect of the substituents *X* on nucleophilic addition appears small when compared to the well known directive effects of the same substituents in nucleophilic reaction of the chromium and manganese complexes.^{10,11}

Carbanion Addition. For applications to synthesis carbon nucleophiles are the most important nucleophiles to be added to disubstituted benzene cyclopentadienyliron cations. Thus, to evaluate further the possible effects of various factors that may influence the site of carbanion addition, we have examined the reaction of some carbanions with a series of disubstituted benzene cyclopentadienyliron cations. Table 1 and 2 present the results. While we have not proven that the products mixtures are the result of kinetic control, shorter or longer reaction times do not alter the product ratios.

For entries 4, 5, 6, 7, 8, and 9, the reactions gave the expected cyclohexadienyl complexes. However, the corresponding cyclohexadienyl complexes were unstable, and decomposed rapidly in the presence of air. We could not isolate the cyclohexadienyl compounds purely, and tried to liberate the organic moieties.

Sutherland^{5f} obtained the alkylated benzene by the pyrolytic cleavage of the cyclohexadienyl cyclopentadienyliron compounds. However, the pyrolytic cleavage was not successful in our cases. Instead, stirring of the cyclohexadienyl complex in cyclohexane for 3 days at room temperature gave the expected mono-functionalized arene compound.

The carbanions were added the less hindered position (C-4) with *o*-dimethoxybenzene (entries 4, 7). This result is rather different from the hydride addition reaction. The difference might be from the steric effect of the carbanion. The reactivity of $[(o\text{-dimethoxybenzene})\text{FeCp}]\text{PF}_6$ is somewhat different from those observed for $(o\text{-dimethoxybenzene})\text{Cr}(\text{CO})_3$ and $(o\text{-dimethoxybenzene})\text{Mn}(\text{CO})_3^+$ previously reported.^{10b,12} Reaction of $(o\text{-dimethoxybenzene})\text{Cr}(\text{CO})_3$ with LiCH_2CN in THF resulted in the addition to C-3. With sterically more demanding anion, LiCMe_2CN , the 1,2,3-isomer was obtained in 85% yield and the less crowded

Table 1. Reaction of Carbanions with (Arene)FeCp⁺ Cations

Entry	Arene	Carbanion	Product ^a	Combined yield (%) ^b
4	<i>o</i> -dimethoxybenzene	LiCH ₂ CN		34
5	<i>m</i> -dimethoxybenzene	LiCH ₂ CN		34
6	<i>p</i> -dimethoxybenzene	LiCH ₂ CN		27
7	<i>o</i> -dimethoxybenzene	LiCMe ₂ CN		60
8	<i>m</i> -dimethoxybenzene	LiCMe ₂ CN		51
9	<i>p</i> -dimethoxybenzene	LiCMe ₂ CN		55

^aThe isomers ratio was determined by ¹H NMR. ^bIsolated yield, but not optimized.**Table 2.** Reactions of LiCMe₂CN with (Arene)FeCp⁺ Cations

Entry	Arene	Carbanion	Product ^a	Combined yield (%) ^b
10	<i>p</i> -bromotoluene	LiCMe ₂ CN		59
11	<i>o</i> -dichlorobenzene	LiCMe ₂ CN		80
12	<i>m</i> -dichlorobenzene	LiCMe ₂ CN		75
13	<i>p</i> -dichlorobenzene	LiCMe ₂ CN		85

1,2,4-isomer was obtained 13% yield.

The carbanions were added C-4 and C-5 positions with *m*-dimethoxybenzene (entries 5 and 8). The ratio of 5A and 5B was determined by ^1H NMR to be 3:2. The ratio of 8A and 8B was 1:2. The isomer ratio was reversed as the carbanion became bulkier. The product distribution would be related to the steric bulkiness of carbanion. Comparing with the hydride addition, the ortho-addition to both methoxy groups was not formed. The result is rather different from the carbanion addition to (*m*-dimethoxybenzene) $\text{Cr}(\text{CO})_3$.^{10b} The anion of the cyanohydrinacetal of valeraldehyde was added exclusively to C-5 for the chromium case.

The carbanions were added to C-2 position with *p*-dimethoxybenzene (entries 6 and 9).

Dialkoxyarene ligands appeared to be somewhat less reactive than anisole, smooth additions were achieved using stabilized anion such as LiCH_2CN and LiCMe_2CN . The isolated yield for monofunctionalized arene was rather low due to some reactions on the silica gel. If we could find a proper demetalation procedure, the isolated yield would be much improved. The yield was rather improved as the carbanion became bulkier and more basic. Generally, the cyclohexadienyl complexes with dimethoxy substituents are unstable than those with a methoxy substituent or without a methoxy substituent.

For entries 10, 11, 12 and 13, the reactions gave the expected cyclohexadienyl complexes. The cyclohexadienyl complexes were stable and could be handled in the air for several hours. The methyl substituent is only weakly electron donating and the free valency effect¹³ favoring *o*-addition could be significant (entry 10). The carbanion was added to C-3 and C-4 with *o*-dichlorobenzene (entry 11). The ratio of 11A and 11B was determined to be 3.1:1. The carbanion was added to C-2, C-4, and C-5 with *m*-dichlorobenzene (entry 12). The ratio of 12A, 12B, and 12C was determined to be 8.7:4.3:1. The carbanion was added to C-2 with *p*-dichlorobenzene (entry 13). The results of the above were identical to the results of hydride addition.^{4a}

The addition of carbanion to $[(\text{dichloroarene})\text{FeCp}]^+$ was shown to be subject to the same directive influences for the hydride addition, itself.

In this work we demonstrated that dialkoxyarene ligands were somewhat less reactive than anisole ligand and smooth addition reactions were achieved with LiCH_2CN and LiCMe_2CN . The directive effects of substituents were rather small compared to other metal systems, such as (arene) $\text{Cr}(\text{CO})_3$ and (arene) $\text{Mn}(\text{CO})_3^+$.^{10,11} This diminishes the utility of the cyclopentadienyliron complexes in the synthetic applications. However, we prepared the following substituted arenes in the present work: 2,4-dimethoxyphenylethanonitrile, 3,5-dimethoxyphenylethanonitrile, 3,4-dimethoxyphenylethanonitrile, 2,5-dimethoxyphenylethanonitrile, 2-methyl-2-(2,4-dimethoxyphenyl)propanonitrile, 2-methyl-2-(3,5-dimethoxyphenyl)propanonitrile, 2-methyl-2-(3,4-dimethoxyphenyl)propanonitrile, 2-methyl-2-(2,5-dimethoxyphenyl)propanonitrile.

Acknowledgement. We thank the S.N.U. Daewoo Research Fund for financial support.

References

- (a) D. A. White, *Organomet. Chem. Rec., Sect. A*, **3**, 497 (1968); (b) S. G. Davies, M. L. H. Green and D. M. P. Mingos, *Tetrahedron*, **34**, 3047 (1978).
- L. A. P. Kane-Maguire, E. D. Honig and D. A. Sweigart, *Chem. Rev.*, **84**, 525 (1984), and references therein.
- A. C. Knipe, S. J. McGuinness and W. E. Watts, *J. Chem. Soc. Perkin I*, 193 (1981).
- (a) I. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, (C), 2261 (1968); (b) R. G. Sutherland, *J. Organomet. Chem. Library*, **3**, 311 (1977); (c) J. F. McGreer and W. E. Watts, *J. Organomet. Chem.*, **110**, 103 (1976); (d) J. F. Helling and W. A. Hendrickson, *J. Organomet. Chem.*, **168**, 87 (1979); (e) C. Moinet and E. Raoult, *J. Organomet. Chem.*, **229**, C31 (1982); (f) C. C. Lee, U. S. Gill, M. Iqbal, C. I. Azogu, and R. G. Sutherland, *J. Organomet. Chem.*, **231**, 151 (1982); (g) C. Moinet and E. Raoult, *J. Organomet. Chem.*, **231**, 245 (1982); (h) C. C. Lee, K. J. Demchuck, U. S. Gill, and R. G. Sutherland, *J. Organomet. Chem.*, **247**, 71 (1983); (i) R. I. Chowdhury, C. C. Lee, A. Piorko, and R. G. Sutherland, *Synth. React. Inorg. Met. Org. Chem.*, **15**, 1237 (1985); (j) R. M. G. Roberts and A. S. Wells, *J. Organomet. Chem.*, **317**, 233 (1986); (k) C. C. Lee, R. L. Chowdhury, A. Piorko, and R. G. Sutherland, *J. Organomet. Chem.*, **310**, 391 (1986); (l) R. M. G. Roberts, J. Silver, A. S. Wells, and S. P. Wilkinson, *J. Organomet. Chem.*, **327**, 247 (1987).
- (a) J. C. Boutonnet and E. Rose, *J. Organomet. Chem.*, **221**, 157 (1981); (b) R. G. Sutherland, A. Piorko, U. S. Gill, and C. C. Lee, *J. Heterocyclic Chem.*, **19**, 801 (1982); (c) R. G. Sutherland, R. L. Chowdhury, A. Piorko, and C. C. Lee, *J. Chem. Soc. Chem. Commun.*, 1296 (1985); (d) R. M. Moriarty and U. S. Gill, *Organometallics*, **5**, 253 (1986); (e) R. G. Sutherland, R. L. Chowdhury, A. Piorko, and C. C. Lee, *J. Organomet. Chem.*, **319**, 379 (1987); (f) A. S. Abd-El-Aziz, C. C. Lee, A. Piorko, and R. G. Sutherland, *J. Organomet. Chem.*, **348**, 95 (1988).
- R. G. Sutherland, C. H. Zhang, R. L. Chowdhury, A. Piorko, and C. C. Lee, *J. Organomet. Chem.*, **333**, 367 (1987).
- I. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc. (C)*, 2024 (1969).
- I. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc. (C)*, 116 (1969).
- C. C. Lee, A. S. Abd-El-Aziz, R. L. Chowdhury, U. S. Gill, A. Piorko, and R. G. Sutherland, *J. Organomet. Chem.*, **315**, 79 (1986).
- (a) M. F. Semmelhack, G. R. Clark, R. Farina, and M. Saeman, *J. Am. Chem. Soc.*, **101**, 217 (1979); (b) M. F. Semmelhack and G. Clark, *J. Am. Chem. Soc.*, **99**, 1675 (1977).
- P. L. Pauson and J. A. Segal, *J. Chem. Soc. Dalton Trans.*, 1683 (1975).
- A. J. Pearson and I. C. Richards, *J. Organomet. Chem.*, **258**, C41 (1983).
- D. W. Clark and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, **174**, 199 (1979).