

# A New Class of Diiron Arene Complexes with Disulfide and Diamine Bridges<sup>1</sup>

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The synthesis and characterization of a new class of bis(cyclopentadienyliron) arene complexes of disulfides and diamines with aliphatic and aromatic bridges are presented. Reactions of the aromatic or aliphatic dithiols with a wide range of cyclopentadienyliron complexes of chloroarenes (1a-i), in the presence of potassium carbonate in a 4:1 THF/DMF mixture, led to the formation of the dicationic iron species (3a-k, 7a-s) in high yields. The synthesis of diiron systems with ether/thioether linkages was also found to be successful. In these reactions, 4-hydroxythiophenol (4) was used as an example with various chloroarene complexes to give the bis(cyclopentadienyliron) arene dications with ether/thioether bridges (5a-f). Reactions of chloroarene complexes (1a,g) with 1,6-hexanediamine (8a) resulted in the formation of the diiron complexes 9a,b in very poor yields (28 and 17%, respectively). However, the use of nitroarene complexes (11a-f) as starting materials proved to increase the reaction yields and decreases the reaction time, which minimized product decomposition in the preparation of complexes 9a and 12a-n. The change in the number of methylene groups of the aliphatic diamines from 2 to 6 resulted in an increase in the product yield. Aromatic diamine bridges were also introduced to yield complexes 14a-e in a similar fashion. The proposed synthetic strategy allowed for the synthesis of a larger number of diiron complexes with various heteroatom linkages, while the traditional route to similar complexes (ligand-exchange reaction of ferrocene with the appropriate aromatic compound) proved to be unsuccessful in terms of yield and versatility.

## Introduction

There has been a growing interest in the area of bimetallic complexes due to their catalytic and electrochemical activities.<sup>2</sup> The possibility exists for the metal centers to act cooperatively in the activation of an organic species where monometallics are ineffective. The diiron systems have been investigated as electron reservoirs, in which the electronically modified diiron complexes can act as homogeneous electrocatalysts.<sup>3</sup> Extensive studies on the use of activating metal moieties in organic synthesis have demonstrated the importance of these organometallic reagents and the need for further development of new

types of complexes.<sup>4</sup> The synthesis and characterization of various bimetallic complexes of bis(chromium tricarbonyl), bis(cyclopentadienyliron), and bis(cyclopentadienylruthenium) arenes have been studied.<sup>5</sup> The primary

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method for the synthesis of (arene)bis(cyclopentadienyliron) dications has been ligand-exchange reactions, in which an excess of ferrocene is reacted with aromatic compounds containing two aromatic rings capable of coordinating to the cyclopentadienyliron moiety.<sup>6</sup> This technique suffered from poor yields as well as the difficulty of introducing some functional groups. Until our recent development in the synthesis of bis(cyclopentadienyliron) complexes of arenes containing etheric linkages, the only route to the synthesis of diiron complexes was the ligand-exchange reaction.<sup>7</sup> Many cyclopentadienyliron complexes of arenes with sulfur or nitrogen linkages have been reported, although there are few examples where two heteroatom substituents are attached to the arene ring.<sup>8</sup> Most of these complexes have been prepared via nucleophilic substitution reactions with sulfur-, nitrogen-, or oxygen-containing nucleophiles and substituted chlorobenzene complexes. The first example of these types of complexes was reported in 1967 by Nesmeyanov and co-workers, who reported the displacement of the chloro group in the (chlorobenzene)cyclopentadienyliron cation with O-, S-, and N-containing nucleophiles.<sup>9</sup> The hydrosulfide ion has also been used as a nucleophile in the synthesis of a thiophenol complex.<sup>10</sup> Disubstitution reactions of (dichlorobenzene)cyclopentadienyliron complexes with sulfur nucleophiles have led to the formation of the complexed arenes with two sulfur linkages.<sup>8b</sup> Heterocyclic complexes of cyclopentadienyliron were also prepared from the reaction of the *o*-dichlorobenzene complex and *o*-disubstituted benzene nucleophiles (where the substituents were OH, SH, and/or NH<sub>2</sub>).<sup>11</sup> The X-ray crystal structures of these complexes have been reported.<sup>12</sup> Other metal moieties such as chromium tricarbonyl have been used in the activation of arene systems toward nucleophilic substitution reactions with sulfur nucleophiles.<sup>13</sup> The objective of this paper is the synthesis of bis(cyclopentadienyliron) arene dications with disulfide and diamine bridges.

## Experimental Section

**General Procedures.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Gemini 200 NMR spectrometer, with chemical shifts calculated from the solvent signals. Coupling constants were calculated in hertz. IR spectra were recorded on a Perkin-Elmer Model 781 spectrophotometer. Elemental analyses were performed at the University of Saskatchewan. All new complexes gave satisfactory elemental analyses.

**Starting Materials.** Starting complexes 1a-i were prepared according to previously reported ligand-exchange reactions.<sup>14</sup> Similarly, complexes 11a-f were obtained from their corresponding aniline complexes by oxidation with H<sub>2</sub>O<sub>2</sub> in CF<sub>3</sub>COOH.<sup>8a</sup> Anhydrous aluminum chloride, aluminum powder, ferrocene, ammonium hexafluorophosphate, chloroarenes, anilines, and the sulfur- and nitrogen-containing nucleophiles are commercially available and were used without further purification.<sup>15</sup> All solvents (reagent grade) were used without purification, with the exception of THF, which was distilled over sodium metal under nitrogen.

**Nucleophilic Substitution Reactions. 1. Experimental Procedure for Complexes 3a-k, 5a-f, and 7a-s.** Typically, 1.0 mmol of the appropriate ( $\eta^6$ -arene)( $\eta^5$ -cyclopentadienyl)iron hexafluorophosphate complex was combined with 0.5 mmol of the dinucleophile in a 50-mL round-bottom flask containing 2.5 mmol (0.345 g) of K<sub>2</sub>CO<sub>3</sub> and 10 mL of a 4:1 THF/DMF mixture. The resulting green-gold solution was stirred under an N<sub>2</sub> atmosphere for 16 h at room temperature, while its color changed to a yellow-brown. A standard workup procedure was followed, in which the reaction mixture was filtered through a sintered glass crucible into a 10% (v/v) HCl solution, causing the formation of a granular precipitate. Acetone washings were added to the filtrate, causing dissolution of the product. This solution was then concentrated by evaporation of the acetone under reduced pressure, and the desired diiron complex precipitated as a yellow granular solid upon the addition of a concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. At this point, the product was recovered by filtration and washed with several portions of cold distilled water. After drying for several hours under vacuum, the product was washed with small amounts of diethyl ether and further dried. The resulting products (fine yellow powders) did not require additional purification in most cases.

**2. Experimental Procedure for Complexes 9a,b.** One millimole of the appropriate ( $\eta^6$ -arene)( $\eta^5$ -cyclopentadienyl)iron hexafluorophosphate complex was combined with 0.5 mmol of 1,6-hexanediamine in a 50-mL round-bottom flask containing 30 mL of THF. The reaction mixture was refluxed for 12 h under an N<sub>2</sub> atmosphere. The solution was then allowed to cool and the solvent concentrated to approximately 5 mL under reduced pressure. The resulting orange residue was redissolved in dichloromethane, and to this solution was added 1.0 mmol of NH<sub>4</sub>PF<sub>6</sub> in 20 mL of distilled water. The product was washed once with distilled water and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to yield an orange solid. This solid was collected by suction filtration, washed with diethyl ether, and then dried under vacuum for several hours. Data for complex 9b (0.148 g, 17%):  $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$  1.47 (br s, 4H, CH<sub>2</sub>), 1.68 (m, 4H, CH<sub>2</sub>), 3.24 (m, 4H, CH<sub>2</sub>), 5.00 (s, 5H, Cp), 5.82 (d, *J* 5.9, 4H, Ar H), 6.39 (d, *J* 5.9, 4H, Ar H);  $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$  26.29 (2C, CH<sub>2</sub>), 28.20 (2C, CH<sub>2</sub>), 42.85 (2C, CH<sub>2</sub>), 66.26 (4C, Ar C), 77.82 (5C, Cp), 86.05 (4C, Ar C), 100.85 (2C, quat Ar C), 126.51 (2C, quat Ar C).

**3. Experimental Procedure for Complex 10.** One millimole (0.413 g) of ( $\eta^6$ -1,4-dichlorobenzene)( $\eta^5$ -cyclopentadienyl)iron hexafluorophosphate was combined with a large excess (1.39 g, 12 mmol) of 1,6-hexanediamine in a 50-mL round-bottom flask

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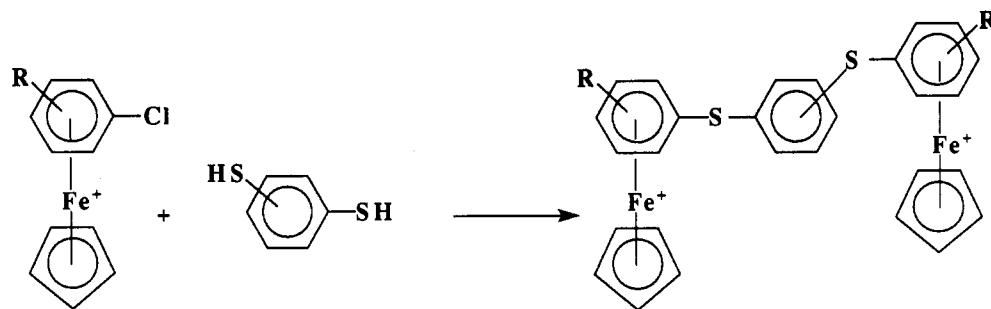
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(15) 1,4-Benzenedithiol was obtained from Professor D. M. McKinnon at the Chemistry Department, University of Manitoba.

Scheme 1



1a R = H  
 b R = 2-CH<sub>3</sub>  
 c R = 3-CH<sub>3</sub>  
 d R = 4-CH<sub>3</sub>  
 e R = 2-Cl  
 f R = 3-Cl  
 g R = 4-Cl  
 h R = 2,6-(CH<sub>3</sub>)<sub>2</sub>  
 i R = 2,5-(CH<sub>3</sub>)<sub>2</sub>

2a 1,2  
 b 1,3  
 c 1,4

3a R = H; 1,2  
 b R = H; 1,3  
 c R = H; 1,4  
 d R = 4-CH<sub>3</sub>; 1,2  
 e R = 4-CH<sub>3</sub>; 1,3  
 f R = 2,6-(CH<sub>3</sub>)<sub>2</sub>; 1,2  
 g R = 2,6-(CH<sub>3</sub>)<sub>2</sub>; 1,3  
 h R = 2,6-(CH<sub>3</sub>)<sub>2</sub>; 1,4  
 i R = 2-Cl; 1,3  
 j R = 2,5-(CH<sub>3</sub>)<sub>2</sub>; 1,4  
 k R = 3-CH<sub>3</sub>; 1,3

Table 1. <sup>1</sup>H NMR Data for Complexes 3a-k

complex no.	δ(acetone-d <sub>6</sub> ), ppm		
	Cp	complexed Ar <sup>a</sup>	others
3a	5.24	6.51 (br s, 10H)	7.59–7.67 (m, 2H, Ar H) 7.72–7.79 (m, 2H, Ar H)
3b	5.22	6.42–6.51 (m, 10H)	7.73–8.05 (m, 4H, Ar H)
3c	5.24	6.40–6.52 (m, 10H)	7.82 (s, 4H, Ar H)
3d	5.20	6.45 (br s, 8H)	2.53 (s, 6H, CH <sub>3</sub> ) 7.48–7.69 (m, 3H, Ar H) 7.85 (d, J 7.3, 1H, Ar H)
3e	5.18	6.40–6.47 (m, 8H)	2.50 (s, 6H, CH <sub>3</sub> ) 7.73–7.94 (m, 4H, Ar H)
3f	5.25	6.55 (m, 2H) 6.64 (m, 4H)	2.71 (s, 12H, CH <sub>3</sub> ) 6.88–6.92 (m, 2H, Ar H) 7.12–7.17 (m, 2H, Ar H)
3g	5.17	6.50–6.60 (m, 6H)	2.57 (s, 12H, CH <sub>3</sub> ) 7.07–7.30 (m, 4H, Ar H)
3h	5.18	6.48 (t, J 6.0, 2H) 6.56 (d, J 5.4, 4H)	2.65 (s, 12H, CH <sub>3</sub> ) 7.14 (s, 4H, Ar H)
3i <sup>b</sup>	5.26	6.26–6.55 (m, 8H)	7.96–8.23 (m, 4H, Ar H)
3j	5.15	6.31 (s, 2H) 6.39 (d, J 5.9, 4H) 6.53 (d, J 6.1, 4H)	2.47 (s, 6H, CH <sub>3</sub> ) 2.64 (s, 6H, CH <sub>3</sub> ) 7.63 (s, 4H, Ar H)
3k	5.17	6.32–6.46 (m, 6H) 6.50 (s, 2H)	7.68–7.75 (m, 2H) 7.82–7.87 (m, 4H) 7.92–7.93 (m, 2H)

<sup>a</sup> J values in hertz. <sup>b</sup> Diastereoisomers present.

containing 10 mL of a 1:1 mixture of THF/DMF and 4 mL of glacial acetic acid. The reaction mixture was then refluxed for 12 h under a nitrogen atmosphere. The resulting disubstituted monoiron complex, 10, was isolated by extracting the product with dichloromethane and adding a concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. The product was washed several times with distilled water to remove the reaction solvents and worked up in the same manner as for complexes 9a,b, yielding 10 (0.283 g, 49%): δ<sub>H</sub>(CD<sub>3</sub>COCD<sub>3</sub>) 1.43–1.65 (m, 8H, CH<sub>2</sub>), 1.69–1.74 (m, 8H, CH<sub>2</sub>), 1.73 (br s, 2H, NH), 3.00 (br s, 4H, NH<sub>2</sub>), 3.12–3.24 (m, 8H, CH<sub>2</sub>), 4.79 (s, 5H, Cp), 5.56 (s, 4H, Ar H); δ<sub>C</sub>(CD<sub>3</sub>COCD<sub>3</sub>) 27.37, 27.71, 29.19, 31.40, 43.83, 51.46 (12, CH<sub>2</sub>), 65.72 (4C, Ar C), 75.71 (5C, Cp), 121.69 (quat Ar C).

**4. Experimental Procedure for Complexes 12a–n.** One millimole of the appropriate (η<sup>6</sup>-nitroarene)(η<sup>5</sup>-cyclopentadienyl)-iron hexafluorophosphate complex was combined with 0.5 mmol of an aliphatic diamine in a 50-mL round-bottom flask containing 2.5 mmol (0.345 g) of K<sub>2</sub>CO<sub>3</sub> and 10 mL of a 1:1 THF/DMF

mixture. The resulting solution was then heated at 60 °C under an N<sub>2</sub> atmosphere for 5 h. The reaction mixture was allowed to cool and was filtered into 10 mL of 10% (v/v) HCl; the reaction flask was washed with dichloromethane, and the washings were filtered. To this was added a concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. The product was then extracted with dichloromethane, and the extract was washed several times with distilled water. After drying over anhydrous magnesium sulfate, the solvent was removed under reduced pressure to yield a brownish-orange oil. The oil was rinsed with diethyl ether and allowed to dry under vacuum for several hours.

**5. Experimental Procedure for Complexes 14a–e.** One millimole of the appropriate (η<sup>6</sup>-nitroarene)(η<sup>5</sup>-cyclopentadienyl)-iron hexafluorophosphate complex was combined with 0.5 mmol of an aromatic diamine (13a,b), and the mixture was added to a 50-mL round-bottom flask containing 2.5 mmol (0.345 g) of K<sub>2</sub>CO<sub>3</sub> and 10 mL of DMF. The resulting solution was then heated at 60 °C under an N<sub>2</sub> atmosphere for 3 h. The final diiron complexes were isolated as oils in the same manner used for the aliphatic complexes.

## Results and Discussion

The synthesis of isomeric (η<sup>6</sup>-phenylenedithio(bis(benzene))bis(η<sup>5</sup>-cyclopentadienyl)iron hexafluorophosphates 3a–k was achieved under mild conditions. Chloroarene complexes 1a–i, isomeric dimercaptobenzenes 2a–c, and potassium carbonate in a THF/DMF (4:1) mixture were stirred for 16 h at room temperature under a nitrogen atmosphere (Scheme 1). Following the workup procedure outlined in the Experimental Section, 3a–k were isolated as yellow solids in high yields (70–95%). The experimental conditions applied in the synthesis of this class of bimetallic complexes with thioether linkages were very mild compared to those used in the traditional synthesis of uncomplexed aromatic thioethers.<sup>16</sup> This is due to the

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Table 2. Yield and  $^{13}\text{C}$  NMR Data for Complexes 3a-k

complex no.	yield, %	$\delta(\text{acetone-}d_6)$ , ppm			
		Cp	complexed Ar	uncomplexed Ar	others
3a	95	79.25	87.81 (2C), 89.12 (8C), 106.41 <sup>b</sup> (2C)	132.24 (2C), 135.35 <sup>b</sup> (2C), 135.98 (2C)	
3b	90	79.19	87.39 (2C), 87.54 (4C), 88.81 (4C), 109.01 <sup>b</sup> (2C),	133.10 <sup>b</sup> (2C), 133.20 (1C), 136.95 (2C), 140.17 (1C)	
3c	70	79.27	87.52 (2C), 87.95 (4C), 88.96 (4C), 108.33 <sup>b</sup> (2C)	132.89 <sup>b</sup> (2C), 136.30 (4C)	
3d	76	79.55	88.78 (4C), 89.41 (4C), 103.86 <sup>b</sup> (2C), 104.42 <sup>b</sup> (2C)	132.06 (2C), 135.57 <sup>b</sup> (2C), 135.70 (2C)	20.16 (2C, CH <sub>3</sub> )
3e	71	79.54	87.29 (4C), 89.16 (4C), 103.42 <sup>b</sup> (2C), 106.72 <sup>b</sup> (2C)	133.05 (1C), 133.19 <sup>b</sup> (2C), 136.39 (2C), 139.51 (1C)	20.16 (2C, CH <sub>3</sub> )
3f	77	79.80	88.57 (2C), 90.02 (4C), 100.02 <sup>b</sup> (2C), 108.25 (4C)	129.02 (2C), 129.19 (2C), 134.49 <sup>b</sup> (2C)	21.27 (4C, CH <sub>3</sub> )
3g	90	79.75	88.73 (2C), 89.98 (4C), 99.12 <sup>b</sup> (2C), 108.29 (4C)	125.18 (1C), 126.59 (2C), 131.74 (1C), 137.42 <sup>b</sup> (2C)	21.16 (4C, CH <sub>3</sub> )
3h	78	79.56	88.36 (2C), 89.84 (4C), 99.53 <sup>b</sup> (2C), 108.28 <sup>b</sup> (4C)	129.81 (4C), 134.25 <sup>b</sup> (2C)	21.28 (4C, CH <sub>3</sub> )
3i <sup>a</sup>	81	81.12, 81.17	86.11 (1C), 86.20 (1C), 87.21 (1C), 87.25 (1C), 87.57 (2C), 89.11 (1C), 89.15 (1C), 110.99 <sup>b</sup> (2C), 111.08 <sup>b</sup> (2C)	131.40 <sup>b</sup> (1C), 133.97 (1C), 138.70 (1C), 141.79 (1C), 142.17 (1C), 142.98 <sup>b</sup> (1C)	
3j <sup>a</sup>	85	79.76	87.99, 88.09 (2C), 89.56, 89.63 (2C), 90.25, 90.31 (2C), 101.75 <sup>b</sup> (2C), 103.74 <sup>b</sup> (2C), 104.67 <sup>b</sup> (1C), 105.09 <sup>b</sup> (1C)	133.43 <sup>b</sup> (2C), 134.64 (2C), 134.84 (2C)	19.54 (2C, CH <sub>3</sub> ), 20.06, 20.10 (2C, CH <sub>3</sub> )
3k <sup>a</sup>	95	78.58	85.41, 85.53 (2C), 87.00, 87.26 (4C), 87.84, 87.93 (2C), 103.71 <sup>b</sup> (2C), 106.49 <sup>b</sup> , 106.61 <sup>b</sup> (2C)	132.17 <sup>b</sup> (1C), 132.28 <sup>b</sup> (1C), 132.25 <sup>b</sup> (1C), 135.41, 135.48 (2C), 138.44, 138.52 (1C)	19.64 (2C, CH <sub>3</sub> )

<sup>a</sup> Diastereoisomers present. <sup>b</sup> Quaternary carbons.

Scheme 2

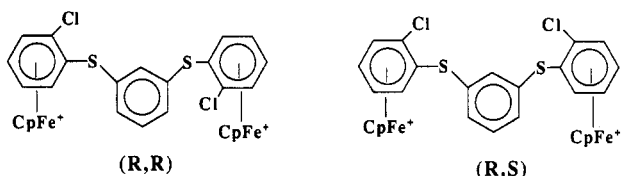
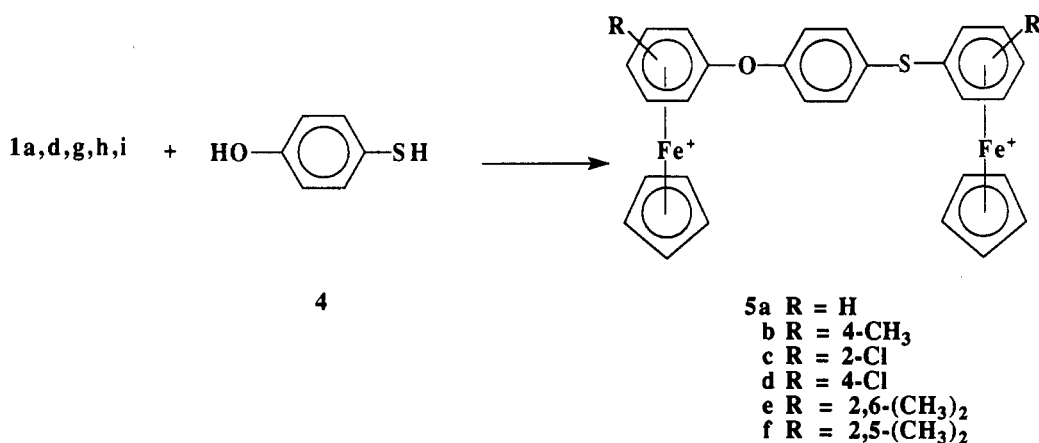


Figure 1. Two possible diastereoisomers of complex 3i.

activation of the chloroarene ring toward nucleophilic aromatic substitution by the complexation with the  $\text{CpFe}^+$  moiety. The identities and yields of the new complexes, 3a-k, are summarized in Tables 1 and 2. The NMR spectra of these complexes clearly indicated all the expected peaks. The elemental analyses of the complexes were fully consistent with the structures indicated. Due to the symmetry of complexes 3a-h, the NMR spectra were quite simple, clearly exhibiting one peak in the proton and carbon NMR spectra for the cyclopentadienyl (Cp) group. The complexed aromatic as well as the uncomplexed aromatic showed one set of peaks, confirming the structures of these complexes. The bridging ligands created in the reactions involving ortho- and meta-substituted starting complexes are prochiral, when considered apart from their  $\text{CpFe}^+$  moieties.<sup>17</sup> When complexed to the iron moieties, the whole molecule becomes chiral. These complexes can be designated as *R,R* or *S,S* (enantiomeric pairs) for one

Table 3.  $^1\text{H}$  NMR Data for Complexes 5a-f

complex no.	$\delta(\text{acetone-}d_6)$ , ppm		
	Cp	complexed Ar <sup>a</sup>	others <sup>a</sup>
5a	5.21	6.36-6.52 (m, 10H)	7.57 (d, <i>J</i> 8.7, 2H, Ar H)
	5.28		7.94 (d, <i>J</i> 8.7, 2H, Ar H)
5b	5.17	6.33 (d, <i>J</i> 6.8, 2H)	2.50 (s, 3H, CH <sub>3</sub> )
	5.24	6.39 (d, <i>J</i> 7.0, 2H)	2.52 (s, 3H, CH <sub>3</sub> )
		6.41 (d, <i>J</i> 6.7, 2H)	7.52 (d, <i>J</i> 8.7, 2H, Ar H)
		6.47 (d, <i>J</i> 7.0, 2H)	7.89 (d, <i>J</i> 8.7, 2H, Ar H)
5c <sup>b</sup>	5.27	6.15-6.65 (m, 6H)	7.71 (d, <i>J</i> 8.8, 2H, Ar H)
	5.28	7.00 (t, <i>J</i> 7.2, 2H)	8.04 (d, <i>J</i> 8.7, 2H, Ar H)
	5.36		
	5.37		
5d	5.31	6.37-6.47 (m, 4H)	7.57 (d, <i>J</i> 8.5, 2H, Ar H)
	5.39	6.64 (d, <i>J</i> 6.8, 2H)	7.93 (d, <i>J</i> 8.5, 2H, Ar H)
		6.81 (d, <i>J</i> 5.9, 2H)	
5e	5.14	6.30-6.42 (m, 4H)	2.70 (s, 6H, CH <sub>3</sub> )
	5.17	6.53 (t, <i>J</i> 6.6, 2H)	2.71 (s, 6H, CH <sub>3</sub> )
			6.80 (d, <i>J</i> 8.7, 2H, Ar H)
5f <sup>b</sup>	5.11	6.14-6.28 (m, 2H)	7.18 (d, <i>J</i> 8.7, 2H, Ar H)
	5.12	6.38 (br s, 2H)	2.44 (s, 3H, CH <sub>3</sub> )
	5.17	6.49 (d, <i>J</i> 5.6, 2H)	2.49 (s, 3H, CH <sub>3</sub> )
	5.18		2.58 (s, 3H, CH <sub>3</sub> )
			2.65 (s, 3H, CH <sub>3</sub> )
		7.43 (d, <i>J</i> 8.4, 2H, Ar H)	
		7.79 (d, <i>J</i> 8.1, 2H, Ar H)	

<sup>a</sup> *J* values in hertz. <sup>b</sup> Diastereoisomers present.

diastereoisomer and *R,S* or *S,R* (enantiomeric pairs) for the other diastereoisomer. As an example, Figure 1 displays the two possible diastereoisomers for  $(\eta^5\text{-1,3-phenylenedithio}bis(2\text{-chlorobenzene}))bis(\eta^5\text{-cyclopentadienyliron})\text{ hexafluorophosphate}$  (3i). Interestingly, the NMR spectra of the 3i,j, complexes showed the presence

(17) (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum Press: New York, 1990; Part A. (b) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* 1970, 9, 371.

Table 4. Yield and  $^{13}\text{C}$  NMR Data for Complexes 5a-f

complex no.	yield, %	$\delta(\text{acetone-}d_6)$ , ppm			
		Cp	complexed Ar	uncomplexed Ar	others
5a	83	78.85, 79.04	78.35 (2C), 85.77 (2C), 86.25 (1C), 86.92 (1C), 87.96 (2C), 88.49 (2C), 111.08 <sup>b</sup> (1C), 126.12 <sup>b</sup> (1C)	123.41 (2C), 133.39 <sup>b</sup> (1C), 139.05 (2C), 156.56 <sup>b</sup> (1C)	
5b	73	78.49, 79.17	77.86 (2C), 85.19 (2C), 87.67 (2C), 88.52 (2C), 101.74 <sup>b</sup> (1C), 102.56 <sup>b</sup> (1C), 108.61 <sup>b</sup> (1C), 126.12 <sup>b</sup> (1C)	122.91 (2C), 131.94 <sup>b</sup> (1C), 138.47 (2C), 156.34 <sup>b</sup> (1C)	19.67 (CH <sub>3</sub> ), 19.89 (CH <sub>3</sub> )
5c <sup>a</sup>	84	80.94, 81.00, 81.50, 81.55	79.64, 79.72 (1C), 85.30, 85.41 (1C), 86.72, 86.77 (1C), 87.34 (1C), 87.50, 87.53 (1C), 87.85, 87.87 (1C), 89.43, 89.46 (1C), 89.58, 89.62 (1C), 99.20, 99.36 <sup>b</sup> (1C), 103.96, 104.04 <sup>b</sup> (1C), 112.73, 112.94 <sup>b</sup> (1C), 125.60, 125.72 <sup>b</sup> (1C)	123.66, 123.81 (2C), 130.41, 130.63 <sup>b</sup> (1C), 140.10, 140.13 (2C), 157.57, 157.63 <sup>b</sup> (1C)	
5d	82	80.53, 81.22	77.98 (2C), 84.70 (2C), 87.71 (2C), 88.38 (2C), 105.06 <sup>b</sup> (1C), 106.10 <sup>b</sup> (1C), 110.87 <sup>b</sup> (1C), 125.70 <sup>b</sup> (1C)	123.33 (2C), 132.54 <sup>b</sup> (1C), 139.05 (2C), 156.33 <sup>b</sup> (1C)	
5e	62	79.19, 79.82	87.74 (2C), 88.47 (4C), 89.43 (4C), 102.24 <sup>b</sup> (1C), 102.54 <sup>b</sup> (2C), 107.44 <sup>b</sup> (2C), 109.28 <sup>b</sup> (1C)	117.42 (2C), 123.48 <sup>b</sup> (1C), 132.84 (2C), 158.16 <sup>b</sup> (1C)	20.01 (2C, CH <sub>3</sub> ), 21.54 (2C, CH <sub>3</sub> )
5f <sup>a</sup>	91	78.92, 79.47	80.01, 80.02 (1C), 85.99, 86.04 (1C), 87.07, 87.14 (1C), 87.70 (1C), 88.66 (1C), 89.05, 89.10 (1C), 93.35, 93.54 <sup>b</sup> (1C), 99.57, 99.83 <sup>b</sup> (1C), 102.42 <sup>b</sup> (1C), 102.97 <sup>b</sup> (1C), 107.50, 107.83 <sup>b</sup> (1C), 126.46 <sup>b</sup> (1C)	122.06, 122.21 (2C), 130.09, <sup>b</sup> 130.33 <sup>b</sup> (1C), 137.51, 137.57 (2C), 156.81, <sup>b</sup> 156.90 <sup>b</sup> (1C)	19.28 (CH <sub>3</sub> ), 19.84 (CH <sub>3</sub> ), 19.91 (CH <sub>3</sub> ), 19.97 (CH <sub>3</sub> )

<sup>a</sup> Diastereoisomers present. <sup>b</sup> Quaternary carbons.

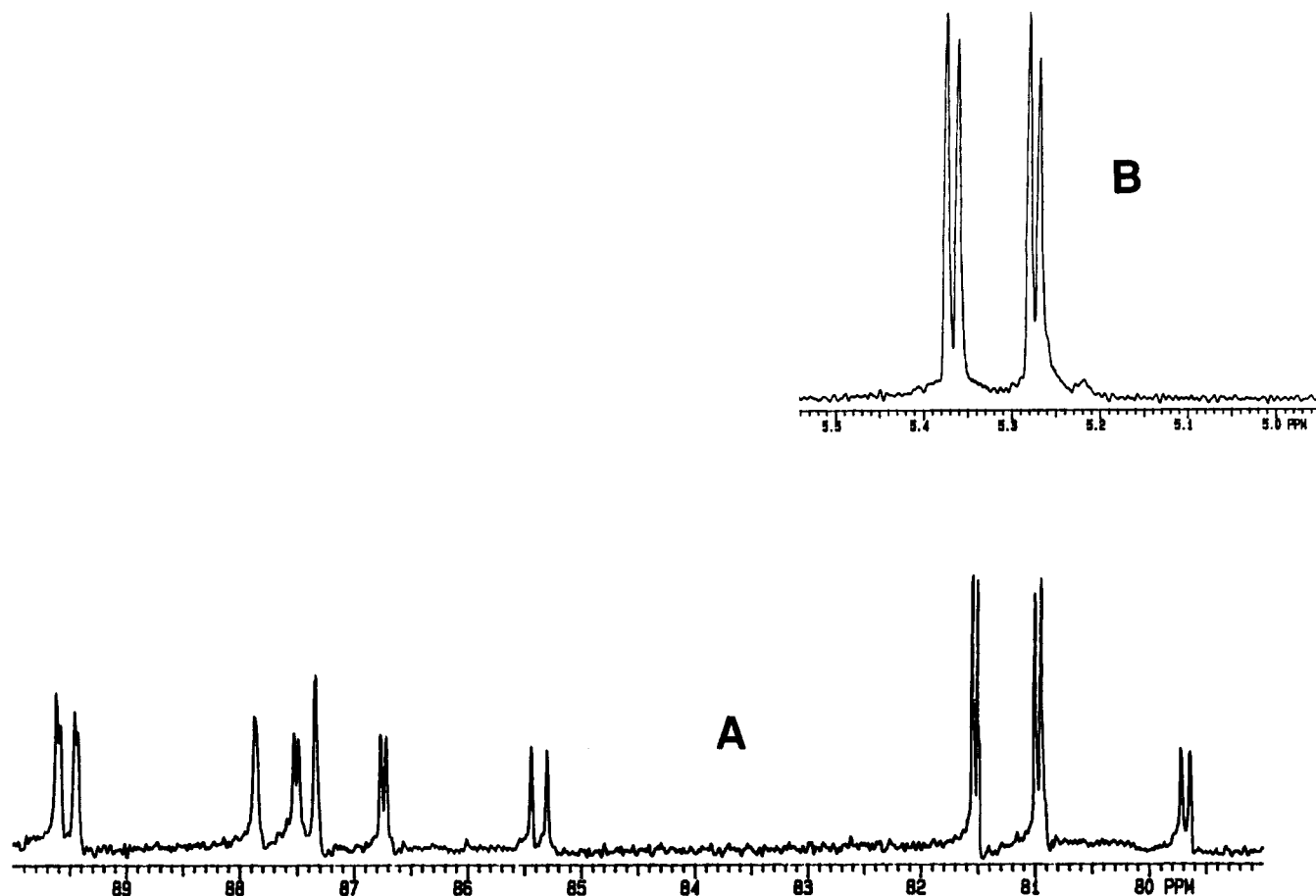


Figure 2. NMR spectra (acetone- $d_6$ ) of complex 5c: (A)  $^{13}\text{C}$  at 50.3 MHz; (B)  $^1\text{H}$  at 200 MHz.

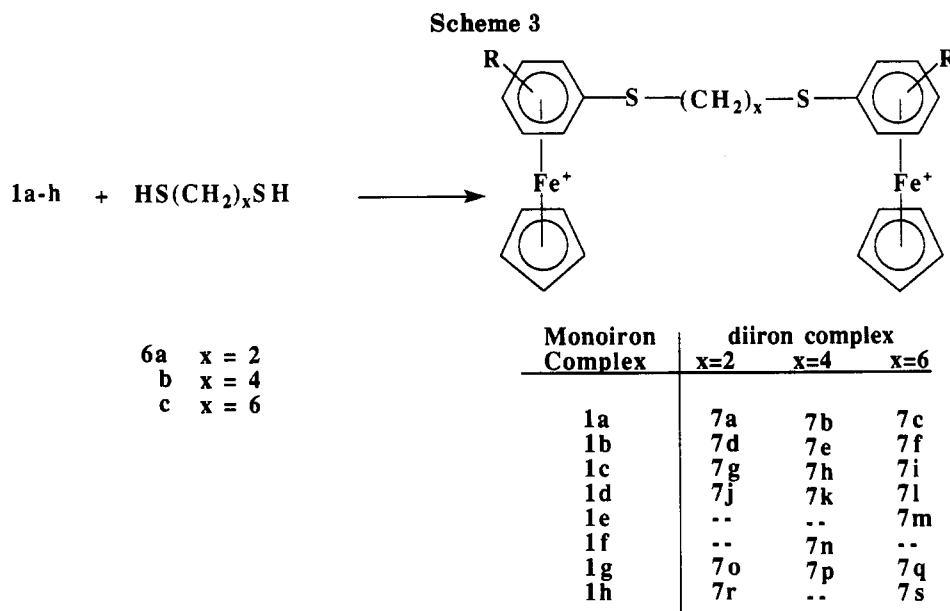
of two diastereoisomers. The ratios of these two isomers were calculated from the  $^1\text{H}$  NMR and appeared to be approximately equal. The  $^{13}\text{C}$  NMR spectrum of complex 3k also clearly showed the presence of two diastereoisomers as indicated in Table 2.

Bis(cyclopentadienyliron) complexes of arenes with mixed ether/thioether linkages, were prepared as described above (Scheme 2). In this investigation, we carried out the reaction with 4-hydroxythiophenol (4). The reactions of this dinucleophile with various selected examples of chloroarene complexes produced the mixed-linkage diiron systems 5a-f in high yield. The NMR data and yields of complexes 5a-f are presented in Tables 3 and 4. The peaks in the NMR spectra of these complexes were assigned on the basis of the prior analyses of the symmetric

complexes.<sup>18</sup> The NMR spectra of complex 5c clearly exhibited the presence of the two diastereoisomers. Figure 2 shows parts of the proton and carbon NMR spectra of complex 5c. In Figure 2A, it is important to note the presence of four different peaks for the Cp carbons in the 80.94–81.55 ppm range. As well, the  $^{13}\text{C}$  NMR showed two sets of peaks confirming the presence of two diastereoisomers. The  $^1\text{H}$  NMR spectra were more complex; nevertheless, the Cp protons appeared as four peaks, as shown in Figure 2B.

In the course of our investigations into the preparation of bis(cyclopentadienyliron) arene complexes with etheric

(18) The NMR data for the symmetric ( $\eta^6$ -phenylenedioxybis(substituted benzene))bis(cyclopentadienyliron) are summarized in ref 7a.

**Table 5.**  $^1H$  NMR Data for Complexes 7a-s

complex no.	$\delta(\text{acetone-}d_6)$ , ppm			complex no.	$\delta(\text{acetone-}d_6)$ , ppm		
	Cp	complexed Ar <sup>a</sup>	others <sup>a</sup>		Cp	complexed Ar <sup>a</sup>	others <sup>a</sup>
7a	5.21	6.36–6.64 (m, 10H)	3.69 (s, 4H, CH <sub>2</sub> )	7j	5.13	6.41 (d, <i>J</i> 6.4, 4H)	2.49 (s, 6H, CH <sub>3</sub> )
7b	5.17	6.34–6.59 (m, 10H)	2.02 (m, 4H, $\beta$ -CH <sub>2</sub> ) <sup>b</sup>			6.54 (d, <i>J</i> 6.4, 4H)	3.63 (s, 4H, CH <sub>2</sub> )
			3.37 (t, <i>J</i> 7.2, 4H, $\alpha$ -CH <sub>2</sub> )	7k	5.12	6.40 (d, <i>J</i> 6.7, 4H)	1.98 (m, 4H, $\beta$ -CH <sub>2</sub> )
7c	5.16	6.44–6.56 (m, 10H)	1.61 (m, 4H, $\gamma$ -CH <sub>2</sub> )			6.49 (d, <i>J</i> 6.8, 4H)	2.50 (s, 6H, CH <sub>3</sub> )
			1.81 (m, 4H, $\beta$ -CH <sub>2</sub> )				3.38 (t, <i>J</i> 7.2, 4H, $\alpha$ -CH <sub>2</sub> )
			3.29 (t, <i>J</i> 6.9, 4H, $\alpha$ -CH <sub>2</sub> )	7l	5.10	6.44 (m, 8H)	1.60 (m, 4H, $\gamma$ -CH <sub>2</sub> )
7d <sup>c</sup>	5.09	6.30–6.40 (m, 4H)	2.60 (s, 3H, CH <sub>3</sub> )				1.79 (m, 4H, $\beta$ -CH <sub>2</sub> )
	5.10	6.49 (d, <i>J</i> 5.9, 2H)	2.62 (s, 3H, CH <sub>3</sub> )				2.48 (s, 6H, CH <sub>3</sub> )
		6.65 (d, <i>J</i> 6.2, 2H)	3.66 (m, 4H, CH <sub>2</sub> )				3.26 (m, 4H, $\alpha$ -CH <sub>2</sub> )
7e	5.09	6.29 (t, <i>J</i> 5.9, 2H)	2.03 (m, 4H, $\beta$ -CH <sub>2</sub> ) <sup>b</sup>	7m	5.20	6.44–6.48 (m, 4H)	1.68 (m, 4H, $\gamma$ -CH <sub>2</sub> )
		6.40 (t, <i>J</i> 6.0, 2H)	2.59 (s, 6H, CH <sub>3</sub> )			6.75–6.79 (m, 2H)	1.88 (m, 4H, $\beta$ -CH <sub>2</sub> )
		6.48 (d, <i>J</i> 5.9, 2H)	3.38 (m, 4H, $\alpha$ -CH <sub>2</sub> )			6.88–6.92 (m, 2H)	3.37 (t, <i>J</i> 6.6, 4H, $\alpha$ -CH <sub>2</sub> )
		6.62 (d, <i>J</i> 6.3, 2H)		7n	5.27	6.50–6.57 (m, 4H)	1.98 (m, 4H, $\beta$ -CH <sub>2</sub> )
7f	5.07	6.27 (t, <i>J</i> 6.0, 2H)	1.64 (m, 4H, $\gamma$ -CH <sub>2</sub> )			6.59 (d, <i>J</i> 5.8, 2H)	3.44 (m, 4H, $\alpha$ -CH <sub>2</sub> )
		6.38 (t, <i>J</i> 6.2, 2H)	1.84 (m, 4H, $\beta$ -CH <sub>2</sub> )			6.96 (s, 2H)	
		6.47 (d, <i>J</i> 6.2, 2H)	2.58 (s, 6H, CH <sub>3</sub> )	7o	5.30	6.74 (d, <i>J</i> 6.8, 4H)	3.69 (s, 4H, CH <sub>2</sub> )
		6.57 (d, <i>J</i> 6.2, 2H)	3.30 (t, <i>J</i> 6.4, 4H, $\alpha$ -CH <sub>2</sub> )			6.85 (d, <i>J</i> 6.8, 4H)	
7g	5.12	6.30 (d, <i>J</i> 6.1, 2H)	2.55 (s, 6H, CH <sub>3</sub> )	7p	5.28	6.65 (d, <i>J</i> 6.8, 4H)	1.97–2.02 (m, 4H, $\beta$ -CH <sub>2</sub> )
		6.40 (t, <i>J</i> 6.2, 2H)	3.66 (s, 4H, CH <sub>2</sub> )			6.83 (d, <i>J</i> 6.8, 4H)	3.34 (m, 4H, $\alpha$ -CH <sub>2</sub> )
		6.51 (d, <i>J</i> 6.6, 2H)		7q	5.27	6.64 (d, <i>J</i> 6.8, 4H)	1.58 (m, 4H, $\gamma$ -CH <sub>2</sub> )
		6.56 (s, 2H)				6.82 (d, <i>J</i> 6.8, 4H)	1.78 (m, 4H, $\beta$ -CH <sub>2</sub> )
7h	5.11	6.28 (d, <i>J</i> 6.0, 2H)	2.20 (m, 4H, $\beta$ -CH <sub>2</sub> )				3.28 (t, <i>J</i> 7.3, 4H, $\alpha$ -CH <sub>2</sub> )
		6.40 (t, <i>J</i> 6.0, 2H)	2.56 (s, 6H, CH <sub>3</sub> )	7r	5.07	6.37 (t, <i>J</i> 6.9, 2H)	2.78 (s, 12H, CH <sub>3</sub> )
		6.43–6.49 (m, 2H)	3.30–3.41 (m, 4H, $\alpha$ -CH <sub>2</sub> )			6.48 (d, <i>J</i> 5.8, 4H)	3.18 (s, 4H, CH <sub>2</sub> )
		6.52 (s, 2H)		7s	5.09	6.30–6.41 (m, 4H)	1.40 (m, 4H, $\gamma$ -CH <sub>2</sub> )
7i	5.10	6.27 (d, <i>J</i> 5.9, 2H)	1.52 (m, 4H, $\gamma$ -CH <sub>2</sub> )			6.48–6.52 (m, 2H)	1.64 (m, 4H, $\beta$ -CH <sub>2</sub> )
		6.35–6.45 (m, 4H)	1.78 (m, 4H, $\beta$ -CH <sub>2</sub> )				2.83 (s, 12H, CH <sub>3</sub> )
		6.49 (s, 2H)	2.56 (s, 6H, CH <sub>3</sub> )				2.87 (t, <i>J</i> 7.4, 4H, $\alpha$ -CH <sub>2</sub> )
			3.28 (t, <i>J</i> 7.3, 4H, $\alpha$ -CH <sub>2</sub> )				

<sup>a</sup> *J* values in hertz. <sup>b</sup> Signal obscured by solvent peak. <sup>c</sup> Diastereoisomers present.

linkages, we observed that the reaction of chloroarene complexes with dihydroxy aromatic compounds proceeded under very mild conditions, leading to the formation of the dicationic complexes with aromatic ether linkages.<sup>7a</sup> Using this methodology, an attempt was made to use aliphatic diols as nucleophiles. However, this attempt failed to give the desired diiron complexes, due to the higher  $pK_a$  values of the diols in comparison to the phenolic compounds.<sup>19</sup> We have been able to prepare a few diiron complexes with aliphatic diols using a stronger base.<sup>20</sup> In this study, we undertook the investigation with aliphatic

dithiols using the same methodological approach we used in the case of aromatic dithiols, due to the lower  $pK_a$  values of the thiol compounds compared to the aliphatic diols.<sup>21</sup> Scheme 3 shows representative examples of diiron complexes with aliphatic disulfide linkages. Aliphatic dithiols 6a–c were employed as dinucleophiles in the reactions with chloroarene complexes in the presence of a weak base (potassium carbonate), in a mixture of THF/DMF, as described in the Experimental Section. All reactions proceeded very smoothly, leading to the formation of the diiron complexes 7a–s. The NMR data for these complexes are combined in Tables 5 and 6. The presence of

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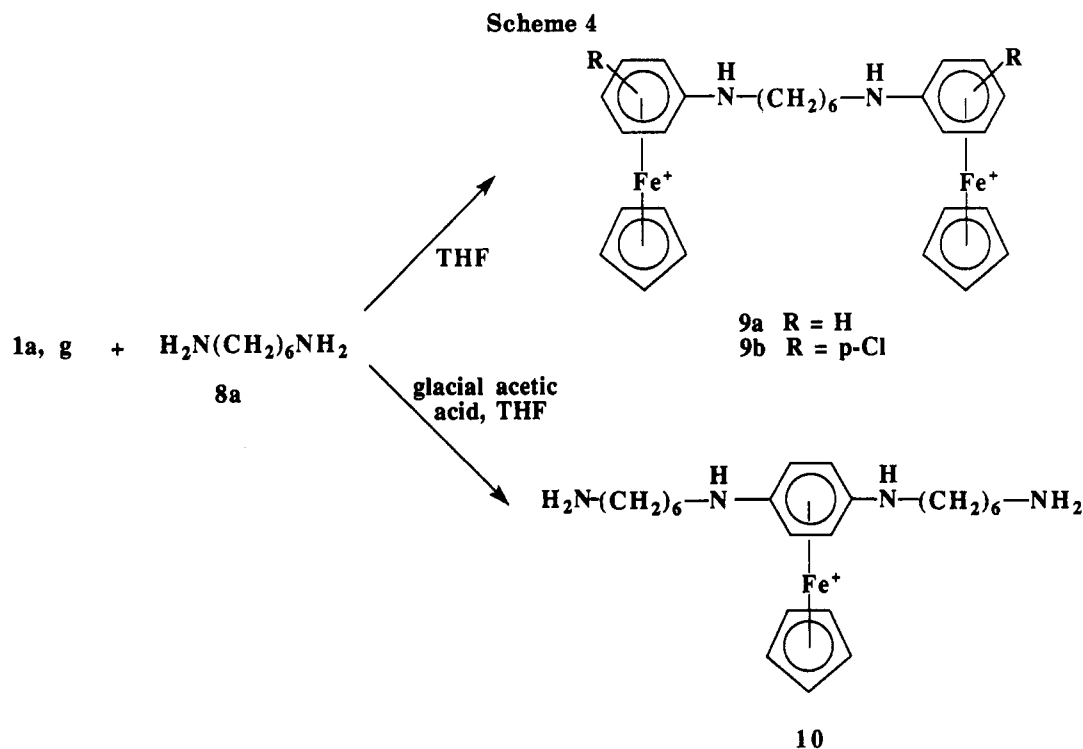
(20) Abd-El-Aziz, A. S.; Lei, Y. Unpublished results.

(21) Fessenden, R. J.; Fessenden, J. S. *Organic Chemistry*, 4th ed.; Brooks/Cole Publishing Co.: CA, 1990; p 315.

Table 6. Yield and  $^{13}\text{C}$  NMR Data for Complexes 7a-s

complex no.	yield, %	$\delta(\text{acetone-}d_6)$ , ppm		
		Cp	complexed Ar	others
7a	82	79.06	87.10 (2C), 87.20 (4C), 88.60 (4C), 108.36 <sup>a</sup> (2C)	32.62 (2C, CH <sub>2</sub> )
7b	82	78.65	85.37 (4C), 86.28 (2C), 88.01 (4C), 110.25 <sup>a</sup> (2C)	28.16 (2C, $\beta$ -CH <sub>2</sub> ), 31.81 (2C, $\alpha$ -CH <sub>2</sub> )
7c	81	78.67	85.14 (4C), 86.16 (2C), 87.98 (4C), 110.77 <sup>a</sup> (2C)	28.47 (2C, $\gamma$ -CH <sub>2</sub> ), 29.42 (2C, $\beta$ -CH <sub>2</sub> ), 32.02 (2C, $\alpha$ -CH <sub>2</sub> )
7d	70	79.15	86.63 (4C), 87.21 (2C), 89.70 (2C), 101.55 <sup>a</sup> (2C), 107.84 <sup>a</sup> (2C)	19.95 (2C, CH <sub>3</sub> ), 32.52 (2C, CH <sub>2</sub> )
7e	75	79.05	84.60 (2C), 85.99 (2C), 86.83 (2C), 89.51 (2C), 100.38 <sup>a</sup> (2C), 110.21 <sup>a</sup> (2C)	19.82 (2C, CH <sub>3</sub> ), 28.00 (2C, $\beta$ -CH <sub>2</sub> ), 31.87 (2C, $\alpha$ -CH <sub>2</sub> )
7f	85	78.98	84.26 (2C), 85.85 (2C), 86.73 (2C), 89.45 (2C), 100.50 <sup>a</sup> (2C), 110.76 <sup>a</sup> (2C)	19.76 (2C, CH <sub>3</sub> ), 28.89 (2C, $\gamma$ -CH <sub>2</sub> ), 29.14 (2C, $\beta$ -CH <sub>2</sub> ), 32.28 (2C, $\alpha$ -CH <sub>2</sub> )
7g	80	79.31	85.40 (2C), 87.46 (2C), 87.86 (2C), 87.95 (2C), 104.36 <sup>a</sup> (2C), 107.60 <sup>a</sup> (2C)	20.54 (2C, CH <sub>3</sub> ), 32.68 (2C, CH <sub>2</sub> )
7h	93	79.16	83.88 (2C), 86.53 (2C), 86.93 (2C), 87.56 (2C), 104.11 <sup>a</sup> (2C), 109.90 <sup>a</sup> (2C)	20.56 (2C, CH <sub>3</sub> ), 28.47 (2C, $\beta$ -CH <sub>2</sub> ), 31.82 (2C, $\alpha$ -CH <sub>2</sub> )
7i	78	78.98	83.47 (2C), 86.04 (2C), 86.67 (2C), 87.37 (2C), 103.78 <sup>a</sup> (2C), 110.26 <sup>a</sup> (2C)	20.42 (2C, CH <sub>3</sub> ), 28.60 (2C, $\gamma$ -CH <sub>2</sub> ), 29.43 (2C, $\beta$ -CH <sub>2</sub> ), 32.07 (2C, $\alpha$ -CH <sub>2</sub> )
7j	79	79.37	86.63 (4C), 88.87 (4C), 102.96 <sup>a</sup> (2C), 106.36 <sup>a</sup> (2C)	20.07 (2C, CH <sub>3</sub> ), 32.73 (2C, CH <sub>2</sub> )
7k	60	79.32	85.14 (4C), 88.65 (4C), 102.51 <sup>a</sup> (2C), 108.78 <sup>a</sup> (2C)	20.10 (2C, CH <sub>3</sub> ), 28.55 (2C, $\beta$ -CH <sub>2</sub> ), 31.93 (2C, $\alpha$ -CH <sub>2</sub> )
7l	80	79.30	84.95 (4C), 88.64 (4C), 102.27 <sup>a</sup> (2C), 109.23 <sup>a</sup> (2C)	20.12 (2C, CH <sub>3</sub> ), 28.67 (2C, $\gamma$ -CH <sub>2</sub> ), 29.05 (2C, $\beta$ -CH <sub>2</sub> ), 32.40 (2C, $\alpha$ -CH <sub>2</sub> )
7m	82	80.67	83.71 (2C), 85.92 (2C), 86.90 (2C), 88.56 (2C), 103.82 <sup>a</sup> (2C), 111.89 <sup>a</sup> (2C)	28.53 (2C, $\gamma$ -CH <sub>2</sub> ), 31.91 (2C, $\beta$ -CH <sub>2</sub> ), 28.80 (2C, $\alpha$ -CH <sub>2</sub> )
7n	78	81.21	84.25 (2C), 85.80 (2C), 86.90 (2C), 87.93 (2C), 107.67 <sup>a</sup> (2C), 111.55 <sup>a</sup> (2C)	28.25 (2C, $\beta$ -CH <sub>2</sub> ), 31.90 (2C, $\alpha$ -CH <sub>2</sub> )
7o	87	81.42	86.41 (4C), 88.72 (4C), 106.45 <sup>a</sup> (2C), 108.17 <sup>a</sup> (2C)	32.50 (2C, CH <sub>2</sub> )
7p	74	81.89	84.46 (4C), 88.21 (4C), 106.05 <sup>a</sup> (2C), 109.50 <sup>a</sup> (2C)	28.29 (2C, $\beta$ -CH <sub>2</sub> ), 31.82 (2C, $\alpha$ -CH <sub>2</sub> )
7q	81	81.25	84.57 (4C), 88.40 (4C), 105.94 <sup>a</sup> (2C), 111.19 <sup>a</sup> (2C)	28.74 (2C, $\gamma$ -CH <sub>2</sub> ), 29.41 (2C, $\beta$ -CH <sub>2</sub> ), 32.31 (2C, $\alpha$ -CH <sub>2</sub> )
7r	77	79.15	87.93 (2C), 89.27 (4C), 101.22 <sup>a</sup> (2C), 108.04 <sup>a</sup> (4C)	21.59 (4C, CH <sub>3</sub> ), 38.14 (2C, CH <sub>2</sub> )
7s	72	79.22	87.90 (2C), 89.37 (4C), 101.52 <sup>a</sup> (2C), 108.24 <sup>a</sup> (4C)	21.65 (4C, CH <sub>3</sub> ), 24.64 (2C, $\gamma$ -CH <sub>2</sub> ), 34.53 (2C, $\beta$ -CH <sub>2</sub> ), 36.36 (2C, $\alpha$ -CH <sub>2</sub> )

<sup>a</sup> Quaternary carbons.

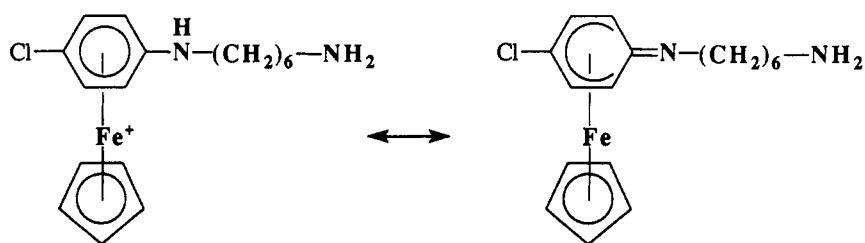


diastereoisomers was noticed in some cases and is reported in these tables. The change in the chain length from two to six methylene groups did not affect the progress of the reaction or the yields of the products. The ability to vary the chain length was important for the development of these bimetallic complexes, which could be used as monomeric units in the synthesis of polymeric materials.<sup>22</sup>

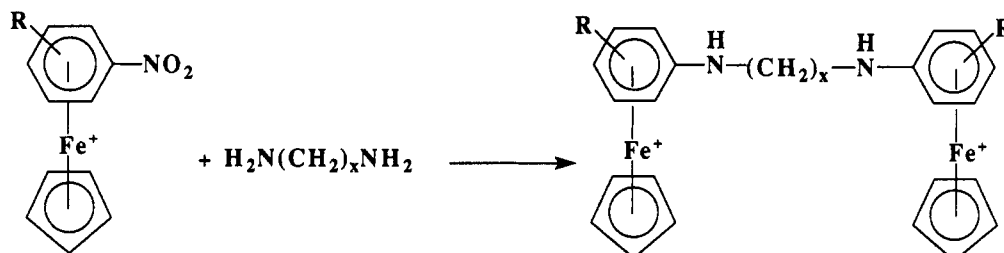
The change of the chain length could vary the properties of the resulting materials in terms of solubility as well as size/charge relationship.

We also investigated the use of diamines as nucleophiles in our search for bis(cyclopentadienyliron) arene complexes with amine bridges. Previous attempts in the synthesis of complexes with certain amine functionalities via ligand-exchange reactions were found to produce the desired complexes in very low yields. ( $\eta^6$ -Diphenylamine)-

Scheme 5



Scheme 6



- 11 a R = H  
 b R = 2-CH<sub>3</sub>  
 c R = 3-CH<sub>3</sub>  
 d R = 4-CH<sub>3</sub>  
 e R = 2,6-(CH<sub>3</sub>)<sub>2</sub>  
 f R = 2,5-(CH<sub>3</sub>)<sub>2</sub>
- 8a x=6  
 8b x=4  
 8c x=2

Monoiron Complex	diiron complex		
	x=2	x=4	x=6
1a	12a	12b	9a
1b	12c	12d	12e
1c	12f	12g	12h
1d	12i	---	12j
1e	12k	12l	12m
1f	---	---	12n

Table 7. <sup>1</sup>H NMR Data for Complexes 9a and 12a-n

complex no.	$\delta(\text{acetone-}d_6)$ , ppm			complex no.	$\delta(\text{acetone-}d_6)$ , ppm			
	Cp	complexed Ar <sup>a</sup>	others <sup>a</sup>		Cp	complexed Ar <sup>a</sup>	others <sup>a</sup>	
9a	4.96	5.81 (d, <i>J</i> 6.6, 4H)	1.51 (m, 4H, $\gamma$ -CH <sub>2</sub> )	12h	4.90	5.73–5.83 (m, 4H)	1.53 (m, 4H, $\gamma$ -CH <sub>2</sub> )	
		5.91–6.09 (m, 4H)	1.74 (m, 4H, $\beta$ -CH <sub>2</sub> )			5.94 (d, <i>J</i> 5.9, 2H)	1.74 (m, 4H, $\beta$ -CH <sub>2</sub> )	
		6.13–6.17 (m, 2H)	3.31 (m, 4H, $\alpha$ -CH <sub>2</sub> )			6.05 (t, <i>J</i> 6.1, 2H)	2.45 (s, 6H, CH <sub>3</sub> )	
12a	5.02	5.92 (d, <i>J</i> 6.6, 4H)	3.74 (d, <i>J</i> 5.3, 4H, $\alpha$ -CH <sub>2</sub> )	12i	4.95	5.85 (d, <i>J</i> 6.9, 4H)	5.83 (br s, 2H, NH)	
		6.07–6.10 (m, 4H)	6.05 (br s, 2H, NH)			6.10 (d, <i>J</i> 6.7, 4H)	2.41 (s, 6H, CH <sub>3</sub> )	
		6.18 (t, <i>J</i> 6.4, 2H)					3.66–3.69 (m, 4H, CH <sub>2</sub> )	
12b	4.98	5.85 (d, <i>J</i> 6.4, 4H)	1.89 (m, 4H, $\beta$ -CH <sub>2</sub> )	12j	4.91	5.75 (d, <i>J</i> 6.9, 4H)	1.50–1.56 (m, 4H, $\gamma$ -CH <sub>2</sub> )	
		6.03 (t, <i>J</i> 5.8, 4H)	3.41 (m, 4H, $\alpha$ -CH <sub>2</sub> )			6.05 (d, <i>J</i> 6.9, 4H)	1.70–1.79 (m, 4H, $\beta$ -CH <sub>2</sub> )	
		6.16 (t, <i>J</i> 5.5, 2H)	5.98 (br s, 2H, NH)				2.40 (s, 6H, CH <sub>3</sub> )	
12c <sup>b</sup>	4.89	5.93–6.04 (m, 4H)	2.41 (s, 3H, CH <sub>3</sub> )	12k <sup>d</sup>	4.90	5.96 (t, <i>J</i> 6.2, 2H)	5.85 (br s, 2H, NH)	
		4.92	6.11–6.21 (m, 4H)			2.42 (s, 3H, CH <sub>3</sub> )	6.20 (d, <i>J</i> 6.0, 4H)	2.57 (s, 12H, CH <sub>3</sub> )
						3.85 (m, 4H, CH <sub>2</sub> )	6.14 (d, <i>J</i> 6.0, 4H)	3.66 (s, 4H, CH <sub>2</sub> )
12d	4.89	5.92 (t, <i>J</i> 6.5, 4H)	1.99 (m, 4H, $\beta$ -CH <sub>2</sub> )	12l <sup>d</sup>	4.87	5.91 (t, <i>J</i> 6.0, 2H)	1.74 (quintet, <i>J</i> 7.3, 4H, $\beta$ -CH <sub>2</sub> )	
		6.10 (d, <i>J</i> 6.5, 2H)	2.40 (s, 6H, CH <sub>3</sub> )			6.14 (d, <i>J</i> 6.0, 4H)	2.55 (s, 12H, CH <sub>3</sub> )	
		6.15 (d, <i>J</i> 5.9, 2H)	3.49 (m, 4H, $\alpha$ -CH <sub>2</sub> )				3.41 (t, <i>J</i> 6.5, 4H, $\alpha$ -CH <sub>2</sub> )	
12e	4.88	5.84–5.94 (m, 4H)	1.56 (m, 4H, $\gamma$ -CH <sub>2</sub> )	12m <sup>d</sup>	4.88	5.90 (t, <i>J</i> 5.9, 2H)	1.42 (m, 4H, $\gamma$ -CH <sub>2</sub> )	
		6.06–6.16 (m, 4H)	1.80 (m, 4H, $\beta$ -CH <sub>2</sub> )			6.13 (d, <i>J</i> 6.0, 4H)	1.65 (m, 4H, $\beta$ -CH <sub>2</sub> )	
			2.40 (s, 6H, CH <sub>3</sub> )				2.56 (s, 12H, CH <sub>3</sub> )	
12f	4.93	5.62–6.11 (m, 8H)	3.41 (m, 4H, $\alpha$ -CH <sub>2</sub> )	12n <sup>d</sup>	4.82	5.84–5.88 (m, 4H)	1.55 (m, 4H, $\gamma$ -CH <sub>2</sub> )	
			5.56 (br s, 2H, NH)			6.07 (d, <i>J</i> 6.0, 2H)	1.82 (m, 4H, $\beta$ -CH <sub>2</sub> )	
			5.95 (br s, 2H, NH) <sup>c</sup>				2.36 (s, 6H, CH <sub>3</sub> )	
12g	4.90	5.73–5.81 (m, 2H)	1.87 (quintet, <i>J</i> 6.8, 4H, $\beta$ -CH <sub>2</sub> )			5.95 (br s, 2H, NH) <sup>c</sup>	2.46 (s, 6H, CH <sub>3</sub> )	
		5.94 (d, <i>J</i> 5.9, 2H)	2.45 (s, 6H, CH <sub>3</sub> )			6.06 (t, <i>J</i> 6.3, 2H)	3.41 (m, 4H, $\alpha$ -CH <sub>2</sub> )	
		6.06 (t, <i>J</i> 6.3, 2H)	5.84 (br s, 2H, NH) <sup>c</sup>				5.45 (br s, 2H, NH)	

<sup>a</sup> *J* values in hertz. <sup>b</sup> Diastereoisomers present. <sup>c</sup> NH overlaps with aromatic. <sup>d</sup> NH unobserved.

( $\eta^5$ -cyclopentadienyliron) hexafluorophosphate could be prepared, but in only 6% yield.<sup>23</sup> A number of arene complexes with amine groups, including heterocyclic

complexes, have been prepared using nucleophilic substitution reactions.<sup>24</sup> Reactions with aromatic amines proceeded to give the diphenylamine only if nitroarene

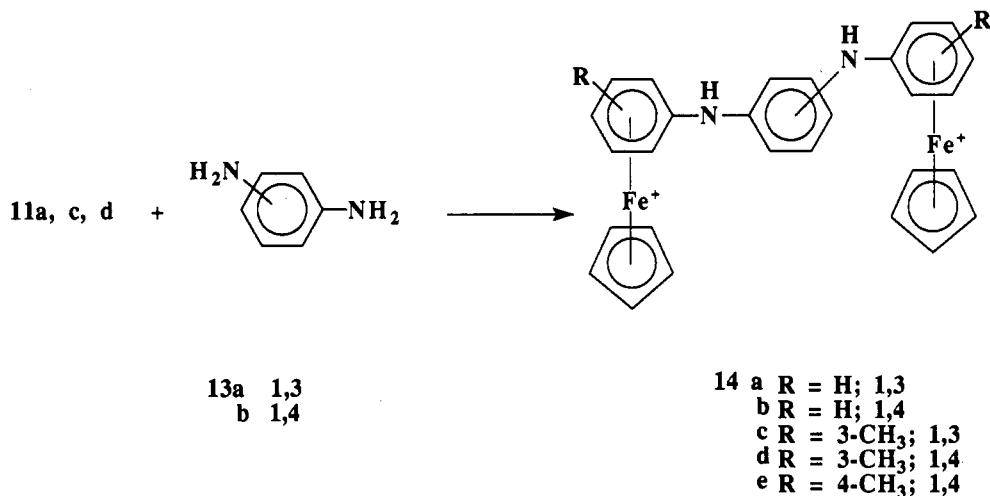


Table 8. Yield,  $^{13}\text{C}$  NMR, and IR Data for Complexes 9a and 12a-n

complex no.	yield, %	$\delta(\text{acetone-}d_6)$ , ppm			IR $\nu_{\text{NH}}$ , $\text{cm}^{-1}$
		Cp	complexed Ar	others	
9a	78	75.34	67.54 (4C), 80.34 (2C), 85.77 (4C), 126.55 <sup>b</sup> (2C)	26.32 (2C, $\gamma$ -CH <sub>2</sub> ), 28.39 (2C, $\beta$ -CH <sub>2</sub> ), 42.61 (2C, $\alpha$ -CH <sub>2</sub> )	3405
12a	48	76.26	68.99 (4C), 81.57 (2C), 86.61 (4C), 126.53 <sup>b</sup> (2C)	42.36 (2C, CH <sub>2</sub> )	3435
12b	62	76.17	68.51 (4C), 81.19 (2C), 86.62 (4C), 127.37 <sup>b</sup> (2C)	26.77 (2C, $\beta$ -CH <sub>2</sub> ), 43.28 (2C, $\alpha$ -CH <sub>2</sub> )	3420
12c <sup>a</sup>	44	76.75	66.71 (1C), 66.87 (1C), 80.82 (2C), 83.01 <sup>b</sup> (2C), 85.27 (2C), 88.99 (2C), 126.13 <sup>b</sup> (2C)	17.75 (CH <sub>3</sub> ), 17.80 (CH <sub>3</sub> ), 42.33, 42.53 (2C, CH <sub>2</sub> )	3440
12d	63	76.46	66.16 (2C), 80.26 (2C), 83.27 <sup>b</sup> (2C), 85.07 (2C), 88.71 (2C), 126.03 <sup>b</sup> (2C)	17.64 (2C, CH <sub>3</sub> ), 26.66 (2C, $\beta$ -CH <sub>2</sub> ), 43.47 (2C, $\alpha$ -CH <sub>2</sub> )	3435
12e	70	76.18	65.63 (2C), 79.90 (2C), 82.85 <sup>b</sup> (2C), 84.78 (2C), 88.47 (2C), 125.96 <sup>b</sup> (2C)	17.54 (2C, CH <sub>3</sub> ), 26.98 (2C, $\gamma$ -CH <sub>2</sub> ), 28.91 (2C, $\beta$ -CH <sub>2</sub> ), 43.31 (2C, $\alpha$ -CH <sub>2</sub> )	3440
12f	46	76.60	67.60 (2C), 70.36 (2C), 82.03 (2C), 85.89 (2C), 102.09 <sup>b</sup> (2C), 126.18 <sup>b</sup> (2C)	20.65 (2C, CH <sub>3</sub> ), 42.46 (2C, CH <sub>2</sub> )	3420
12g	89	76.33	66.90 (2C), 69.69 (2C), 81.48 (2C), 85.65 (2C), 101.84 <sup>b</sup> (2C), 126.65 <sup>b</sup> (2C)	20.57 (2C, CH <sub>3</sub> ), 26.62 (2C, $\beta$ -CH <sub>2</sub> ), 43.15 (2C, $\alpha$ -CH <sub>2</sub> )	3420
12h	43	76.21	66.72 (2C), 69.52 (2C), 81.32 (2C), 85.55 (2C), 101.74 <sup>b</sup> (2C), 126.74 <sup>b</sup> (2C)	20.52 (2C, CH <sub>3</sub> ), 26.93 (2C, $\gamma$ -CH <sub>2</sub> ), 29.05 (2C, $\beta$ -CH <sub>2</sub> ), 43.34 (2C, $\alpha$ -CH <sub>2</sub> )	3425
12i	30	76.73	68.22 (4C), 86.85 (4C), 96.77 <sup>b</sup> (2C), 125.51 <sup>b</sup> (2C)	19.64 (2C, CH <sub>3</sub> ), 42.40 (2C, CH <sub>2</sub> )	3415
12j	71	76.65	67.71 (4C), 86.84 (4C), 96.39 <sup>b</sup> (2C), 126.37 <sup>b</sup> (2C)	19.66 (2C, CH <sub>3</sub> ), 27.17 (2C, $\gamma$ -CH <sub>2</sub> ), 29.26 (2C, $\beta$ -CH <sub>2</sub> ), 43.54 (2C, $\alpha$ -CH <sub>2</sub> )	3420
12k	17	77.77	82.78 (2C), 88.66 (4C), 97.27 <sup>b</sup> (4C), 107.78 <sup>b</sup> (2C)	19.70 (4C, CH <sub>3</sub> ), 48.45 (2C, CH <sub>2</sub> )	3415
12l	22	77.97	82.59 (2C), 88.99 (4C), 89.14 <sup>b</sup> (4C), 126.09 <sup>b</sup> (2C)	18.07 (4C, CH <sub>3</sub> ), 29.29 (2C, $\beta$ -CH <sub>2</sub> ), 48.34 (2C, $\alpha$ -CH <sub>2</sub> )	3430
12m	28	77.53	82.07 (2C), 88.58 (4C), 88.48 <sup>b</sup> (4C), 125.84 <sup>b</sup> (2C)	19.76 (4C, CH <sub>3</sub> ), 27.22 (2C, $\gamma$ -CH <sub>2</sub> ), 31.61 (2C, $\beta$ -CH <sub>2</sub> ), 48.18 (2C, $\alpha$ -CH <sub>2</sub> )	3440
12n	44	76.90	67.71 (2C), 80.62 (2C), 81.74 <sup>b</sup> (2C), 87.99 (2C), 100.71 <sup>b</sup> (2C), 125.74 <sup>b</sup> (2C)	17.35 (2C, CH <sub>3</sub> ), 20.51 (2C, CH <sub>3</sub> ), 27.35 (2C, $\gamma$ -CH <sub>2</sub> ), 29.37 (2C, $\beta$ -CH <sub>2</sub> ), 43.72 (2C, $\alpha$ -CH <sub>2</sub> )	3438

<sup>a</sup> Diastereoisomers present. <sup>b</sup> Quaternary carbons.

Scheme 7



complexes were used as starting materials, as opposed to the chloroarene complexes.<sup>24,25</sup> In this study, we examined the reaction of chloroarene 1a or 1g with 1,6-hexanediamine (8a). Using a 2:1 molar ratio of the complexed arene to the diamine, in the presence of potassium carbonate in THF, resulted in the formation of the diiron species with an aliphatic diamine bridge in low yields. On the other hand, using an excess of the diamine to the 1,4-dichloroarene complex, 1g, in the presence of glacial acetic acid led to double nucleophilic substitution, as shown in Scheme 4. In an earlier study, it was proposed that under the basic experimental conditions, the monosubstituted product with the diamine would deprotonate to give the zwitterion-cyclohexadienyl complex, as described in Scheme 5.<sup>26</sup> This zwitterion is electron rich and prevents further substitution of the second chloro group. The addition of glacial acetic acid prevented the deprotonation, allowing for the second substitution to occur.

Nucleophilic substitution reactions of ethylenediamine with (chlorobenzene)- or isomeric (chlorotoluene)cyclopentadienyliron complexes showed that long reaction times resulted in poor yields and impure products.<sup>8e</sup> In our study, similar behavior was noticed. This led to poor yields and, occasionally, decomposition of the products. Reactions of 1,6-hexanediamine with chlorobenzene and 1,4-dichlorobenzene complexes gave the expected diiron complexes in yields of 28 and 17%, respectively. We have used nitroarene complexes (11a-f) as starting materials since the nitro group is a better leaving group than chlorine. This allowed us to decrease the reaction time to 3-5 h to prevent decomposition of the starting material and the products. Having established the experimental conditions for the synthesis of diiron complexes with diamine linkages, we carried out a number of reactions with selected arene complexes, as well as with three aliphatic diamines with different methylene chains. Scheme 6 represents these examples. The arene complexes reacted with the diamines to produce the desired complexes. Note that increasing the number of the methylene groups in the chain from 2

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Table 9.  $^1\text{H}$  NMR Data for Complexes 14a-e

complex no.	$\delta(\text{acetone-}d_6)$ , ppm			complex no.	$\delta(\text{acetone-}d_6)$ , ppm		
	Cp	complexed Ar <sup>a</sup>	others <sup>a</sup>		Cp	complexed Ar <sup>a</sup>	others <sup>a</sup>
14a	5.06	6.14–6.26 (m, 6H)	7.20–7.37 (m, 3H, Ar H)	14d <sup>b</sup>	4.91	6.25 (d, <i>J</i> 6.1, 4H)	7.82 (d, <i>J</i> 7.5, Ar H)
		6.29–6.36 (m, 4H)	7.59 (t, <i>J</i> 8.0, Ar H)			6.31 (s, 2H)	7.90 (d, <i>J</i> 7.5, Ar H)
14b	5.03	6.31–6.40 (m, 6H)	8.11 (br s, 2H, NH)	14e	4.95	6.42 (t, <i>J</i> 6.1, 2H)	7.94 (d, <i>J</i> 7.5, Ar H)
		6.47–6.54 (m, 4H)	7.10 (d, <i>J</i> 8.8, 2H, Ar H)			6.26 (d, <i>J</i> 6.9, 4H)	8.06 (d, <i>J</i> 7.5, Ar H)
14c	5.01	6.07–6.28 (m, 8H)	5.45 (br s, 2H, NH)			6.41 (d, <i>J</i> 6.8, 4H)	7.82 (d, <i>J</i> 6.7, Ar H)
			2.52 (s, 6H, CH <sub>3</sub> )				7.93 (d, <i>J</i> 7.5, Ar H)
			7.33–7.34 (m, 2H, Ar H)				7.93 (d, <i>J</i> 7.4, Ar H)
			7.58–7.64 (m, 2H, Ar H)				8.03 (d, <i>J</i> 6.9, Ar H)
		8.03 (br s, 2H, NH)					8.06 (br s, 2H, NH)

<sup>a</sup> *J* values in hertz. <sup>b</sup> NH unobserved.

Table 10. Yield,  $^{13}\text{C}$  NMR, and IR Data for Complexes 14a-e

complex no.	yield, %	$\delta(\text{acetone-}d_6)$ , ppm				IR $\nu_{\text{NH}}$ , cm <sup>-1</sup>
		Cp	complexed Ar	uncomplexed Ar	others	
14a	59	77.02	72.49 (4C), 83.06 (2C), 87.26 (4C), 122.30 <sup>a</sup> (2C)	116.96 (1C), 119.66 (2C), 132.24 (1C), 141.44 <sup>a</sup> (2C)		3420
14b	62	77.75	79.28 (4C), 85.30 (2C), 87.34 (4C), 122.42 <sup>a</sup> (2C)	116.26 (2C), 129.15 <sup>a</sup> (1C), 131.69 (2C), 151.19 <sup>a</sup> (1C)		3400
14c	54	77.34	70.84 (2C), 73.82 (2C), 83.46 (2C), 86.51 (2C), 96.93 <sup>a</sup> (2C), 107.97 <sup>a</sup> (2C)	116.88 (1C), 119.48 (1C), 131.47 (1C), 132.18 (1C), 141.53 <sup>a</sup> (2C)	20.83 (2C, CH <sub>3</sub> )	3395
14d	61	78.18	80.50 (2C), 80.58 (2C), 88.03 (2C), 88.81 (2C), 103.65 <sup>a</sup> (2C), 121.03 <sup>a</sup> (2C)	131.27 (2C), 132.23 (2C), 141.53 <sup>a</sup> (1C), 141.63 <sup>a</sup> (1C)	20.54 (2C, CH <sub>3</sub> )	3410
14e	66	78.22	78.75 (4C), 87.55 (4C), 101.52 <sup>a</sup> (2C), 107.81 <sup>a</sup> (2C)	120.15 <sup>a</sup> (2C), 131.08 (2C), 132.22 (2C)	19.80 (2C, CH <sub>3</sub> )	3415

<sup>a</sup> Quaternary carbons.

to 6 resulted in an increase in the yield of the reaction (Table 8). We also observed some steric problems when we used the 2,6-dimethylnitrobenzene complex as a starting material. The yields of these reactions dropped dramatically due to the presence of these two methyl groups ortho to the nitro group. The yields and spectroscopic information are collected and presented in Tables 7 and 8.

Following the investigation with aliphatic amines, we examined the displacement of the nitro group using aromatic diamines as nucleophiles. Scheme 7 shows selected examples of the reactions of 1,3- and 1,4-phenylenediamines, 13a,b, with nitroarene complexes (11a,c,d). Although these reactions proceeded to produce the diiron complexes with aromatic diamine bridges, the reaction with 1,2-phenylenediamine failed to give the desired product but rather gave a mixture of products. The yield, IR, and NMR data are given in Tables 9 and 10.

### Conclusion

Both aliphatic and aromatic dithiols reacted with cyclopentadienyliron complexes of chloroarenes, to form bis(cyclopentadienyliron) arene dications with aliphatic and aromatic dithiol bridges. Diiron complexes with mixed ether/thioether bridges were also prepared using the same synthetic methodology. These types of complexes are important due to their potential use as monomeric species in the synthesis of larger polymeric materials.<sup>22</sup> Also, these

complexes have the potential to act as electron reservoir systems. The above described reactions show clearly that this is a very flexible and efficient route to the synthesis of such complexes in high yields, under very mild conditions. The reactions with aliphatic diamines also proved to be successful when nitroarene complexes were used as starting materials. This was due to the enhancement of the reactivity and the shortening of the reaction times, which minimized the decomposition process. The aromatic diamines were also used to provide a route to the synthesis of diiron complexes with aromatic diamine bridges. This detailed investigation allowed for the synthesis of a new and exciting class of diiron complexes. The application of these complexes in material science should be of great importance. We are currently exploring a wide range of substituents for the synthesis of polymetallic species with one or more heteroatoms. Work is in progress to prepare, characterize, and study the structural features of these complexes.

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