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Cleavage of the Etheric Bond in Cyclopentadienyliron Phenolphthalein Complexes

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Abstract: The reaction of aliphatic primary amines with phenolphthalein-containing dicyclopentadienyliron complexes led to etheric bond cleavage. This unique cleavage reaction is due to nucleophilic attack by the amines *ipso* to the etheric group of the complexed arene, which is activated by coordination to the cationic cyclopentadienyliron moiety.

The role of the cyclopentadienyliron cation in the activation of chloroarenes towards nucleophilic aromatic substitution has been well established.[1] Recently, we have exploited this methodology for the synthesis of cyclic and acyclic polyaryl ethers and thioethers in a step-wise fashion.[2] This work has shown that dicyclopentadienyliron complexes of aromatic ethers may serve as building blocks for the synthesis of oligomeric complexes, prompting us to study further the reactivity of these diiron species.

Phenolphthalein may be reacted with complexes **1-3** to give diiron species **4-6**, as shown in Scheme 1. This was accomplished through the use of a 2:1 molar ratio of the complex to phenolphthalein, in the presence of excess K_2CO_3 in DMF. The mixtures were stirred under nitrogen at room temperature for 16 hours, and the products were isolated as yellow solids in very good yield (93-97%).

Reaction of complexes **4-6** with an excess of a primary amine in DMF at 80°C for 14 hours led to the cleavage of the etheric bonds, as described in Scheme 1. Although etheric cleavage reactions have been briefly reported for chromium tricarbonyl complexes, to date there have been no reports of this bond cleavage for cyclopentadienyliron complexes.[3]

A number of primary amines and diamines were successful in causing cleavage of the etheric bonds of complex **4**. However, reaction of complex **4** with t-butylamine did not result in the formation of the substituted aniline complex, presumably due to the steric effect associated with this amine. As well, reaction with secondary amines resulted only in the isolation of the starting materials. Aromatic amines, such as aniline, did not react, which may be attributed to their relatively low nucleophilicity.

For further confirmation of these structures, photolytic demetallation was used to liberate the free organic amines from the cyclopentadienyliron moiety, as shown in Scheme 1.

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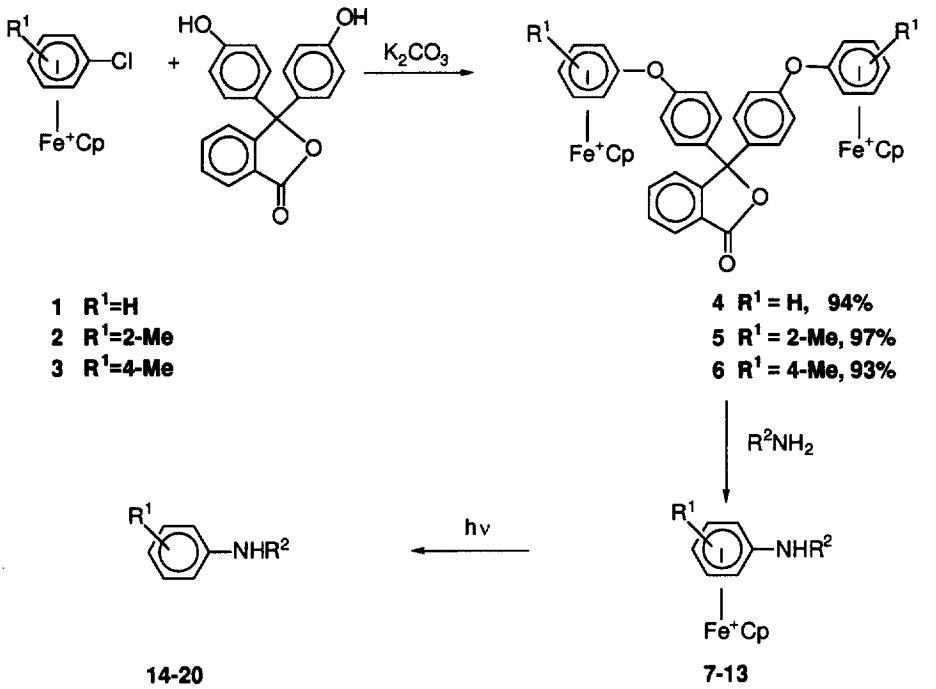
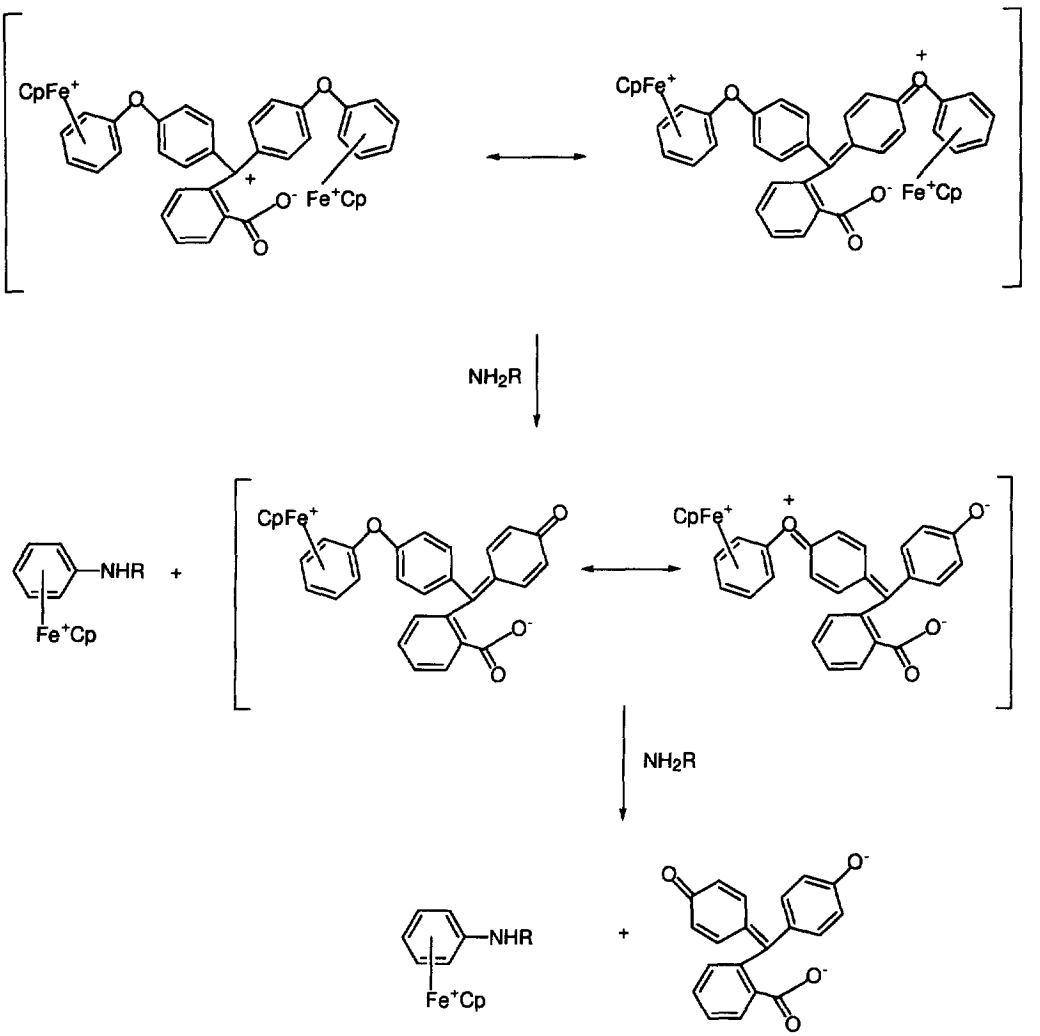


	Yield %		Yield %	R^1	R^2
7	69	**14**	69	H	n-butyl
8	68	**15**	52	H	benzyl
9	42	**16**	46	H	$(CH_2)_2NH_2$
10	54	**17**	43	H	$(CH_2)_4NH_2$
11	68	**18**	45	H	$(CH_2)_6NH_2$
12	63	**19**	74	2-Me	n-butyl
13	66	**20**	75	Me	n-butyl

Scheme 1

We suggest a possible mechanism for this reaction in Scheme 2, in which the lactone ring of the phenolphthalein moiety is opened in basic solution to form a tertiary carbocation. This carbocation is extensively resonance stabilized. Attack of the primary amine *ipso* to each etheric bond results in the liberation of two equivalents of the substituted aniline complex. The presence of phenolphthalein as a side product of this reaction is easily confirmed in the workup procedure. Washing with dilute NaOH solution gives the strong purple colour attributed to the phenolphthalein salt.

This unique reaction allows for the first ever synthesis of compounds **10** and **11**, which cannot be prepared by the previously reported methods.[2b]



Scheme 2

In conclusion, the treatment of dicyclopentadienyliron complexes of arenes containing phenolphthalein bridges with primary amines allowed for the cleavage of etheric bonds. To the best of our knowledge, this is the first example of this type of reaction for cyclopentadienyliron arene complexes. This methodology gives an alternative approach to the synthesis of substituted anilines, which have proven difficult to prepare via nucleophilic aromatic substitution, due to the formation of a neutral zwitterion.[2b,4]

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5. Selected physical data:

   3: ^{1}H NMR: (200 MHz, acetone-D_6): δ = 5.25 (s, 10 H, Cp), 6.31-6.51 (m. 10 H, complexed ArH), 7.42 (d, J = 8.8 Hz, 4H, ArH), 7.62 (d, J = 8.6 Hz, 4H, ArH), 7.80 - 8.05 (m, 4H, ArH); ^{13}C NMR: (50 MHz, acetone-D_6): δ = 78.19 (Cp), 85.94 (complexed ArC), 87.84 (complexed ArC), 90.96 (q), 121.83 (uncomplexed ArC), 125.55 (uncomplexed ArC), 125.77 (q, complexed ArC), 126.55 (uncomplexed ArC), 130.44 (uncomplexed ArC), 131.01 (uncomplexed ArC), 133.86 (q, uncomplexed ArC), 135.98 (uncomplexed ArC), 139.76 (q, uncomplexed ArC), 152.25 (q, uncomplexed ArC), 154.27 (q, uncomplexed ArC), 169.30 (CO).

   6: ^{1}H NMR: (200 MHz, acetone-D_6): δ = 2.82 (s, 1 H, NH), 4.56 (d, J = 6.1 Hz, 2H, CH_2), 4.80 (s, 5H, Cp), 5.88 (d, J = 6.4 Hz, 2H, complexed ArH), 6.03 (t, J = 5.7 Hz, 1H, complexed ArH), 6.17 (t, J = 6.3 Hz, 2H, complexed ArH), 7.45 (m, 5H, ArH); ^{13}C NMR (50 MHz, acetone-D_6): δ = 47.21 (CH_2), 76.18 (Cp), 68.84 (complexed ArC), 81.39 (complexed ArC), 86.66 (complexed ArC), 127.41 (q, complexed ArC), 128.70 (ArC), 128.91 (ArC), 129.73 (ArC), 138.86 (q).

   12: ^{1}H NMR: (200 MHz, acetone-D_6): δ = 4.39 (s, 2H, CH_2), 6.67 (m, 3H, ArH), 7.23 (m, 8H, ArH and NH); ^{13}C NMR (50 MHz, acetone-D_6): δ = 48.62 (CH_2), 139.08 (q), 147.66 (q, ArC).