Pergamon

0277-5387(94)00496-X

Polyhedron Vol. 14, No. 7, pp. 957–960, 1995

0277-5387/95 $9.50+0.00

COMMUNICATION

THE FIRST EXAMPLE OF MULTIPLE OXIDATION REACTIONS OF η^6-ALKYLATED ANILINE-η^5-CYCLOPENTADIENYLIRON COMPLEXES

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(*Received* 18 *October* 1994; *accepted* 25 *November* 1994)

Abstract—A unique synthetic route to cyclopentadienyliron complexes of functionalized nitrobenzene has been developed *via* the successive oxidation of the amine and the alkyl groups of their corresponding aniline complexes. Nucleophilic aromatic substitution reactions of the nitroarene complexes with a number of nucleophiles gave rise to monoiron and diiron complexes with various alkyl and keto substituents.

Since the development of the chemistry of η^6-arene-η^5-cyclopentadienyliron complexes, more attention has been given to the synthesis and reactivities of halogenated arene complexes. This is due to the possibility of using these complexes as starting materials in nucleophilic substitution and addition reactions.[1] The chlorinated arenes could easily undergo ligand exchange reactions with ferrocene leading to the synthesis of the desired complexes.[2] The ease of the synthesis of chloroarene complexes made this route more attractive; however, the need for better leaving groups and for the introduction of various substituents on the arene ring required that we further explore the chemistry of nitroarene complexes. The oxidation procedure for cyclopentadienyliron complexes of aniline and isomeric methylaniline is well established, but only a limited number of nitroarene complexes have been prepared.[3]

We report here the first example of multiple oxidation reactions of alkyl aniline complexes **2a–2d**. The ligand exchange reactions of compounds **1a–1d** with ferrocene ($FeCp_2$) in the presence of $AlCl_3$ and Al powder led to the formation of substituted aniline complexes **2a–2d**, in 56–64% yield (Scheme 1). Subsequent oxidation of any of these complexes with H_2O_2 in CF_3COOH for 2 h at 70°C gave a mixture of products. The NMR studies of this mixture showed the presence of the desired alkyl nitroarene complexes with unexpected arene complexes containing keto groups. This was an important observation which led us to perform time-dependent oxidation studies. Oxidation of 4-ethylaniline for a period of 0.5 h gave the 4-ethylnitrobenzene complex **3a** in a yield of 63%. The most interesting results were obtained following the above oxidation for a period of 24 h. In this case the 4-nitroacetophenone complex was obtained in 42% yield. It should be noted that increasing the reaction time increases the possibility of decomposition reactions, resulting in an even lower yield. This is the first study where a cyclopentadienyliron complex of an alkyl aniline has been oxidized to give a nitrobenzene complex with a keto group directly attached to the aromatic ring. The 4-isopropylnitrobenzene complex was previously prepared and isolated as a trifluoroacetate salt.[4] The X-ray crystal structure of this complex was reported, but neither preparative details nor analytical or spectroscopic data were provided. The oxidation of 4-isopropylaniline complex **2b**, gave the corresponding 4-isopropylnitrobenzene complex **3b**, as well as the 4-nitroacetophenone complex

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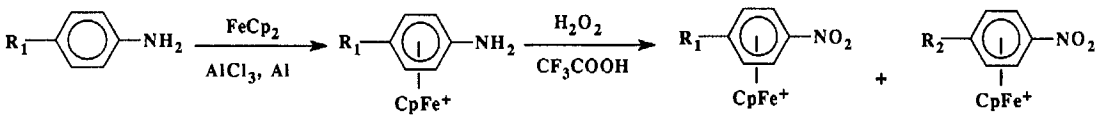


1a $R_1 = CH_2CH_3$
b $R_1 = CH(CH_3)_2$
c $R_1 = CH(CH_3)CH_2CH_3$
d $R_1 = C(CH_3)_3$

2a-d **3a-d**

4a $R_2 = COCH_3$
b $R_2 = COCH_2CH_3$

Scheme 1.

Table 1. Oxidation of alkyl aniline complexes **2a–2d**: reaction times and product yields

Complex	*RT* (h)	Complex	Yield (%)	Complex	Yield (%)
2a R = CH_2CH_3	0.5				
		—	—	**4a**	42
2b R = $CH(CH_3)_2$	0.5				
		—	—	**4a**	53
2c R = $CH(CH_3)CH_2CH_3$	0.5	**3c**	55	—	—
	24[a]	—	—	**4a**	11
		—	—	**4b**	45
2d R = $C(CH_3)_3$	0.5	**3d**	59	—	—

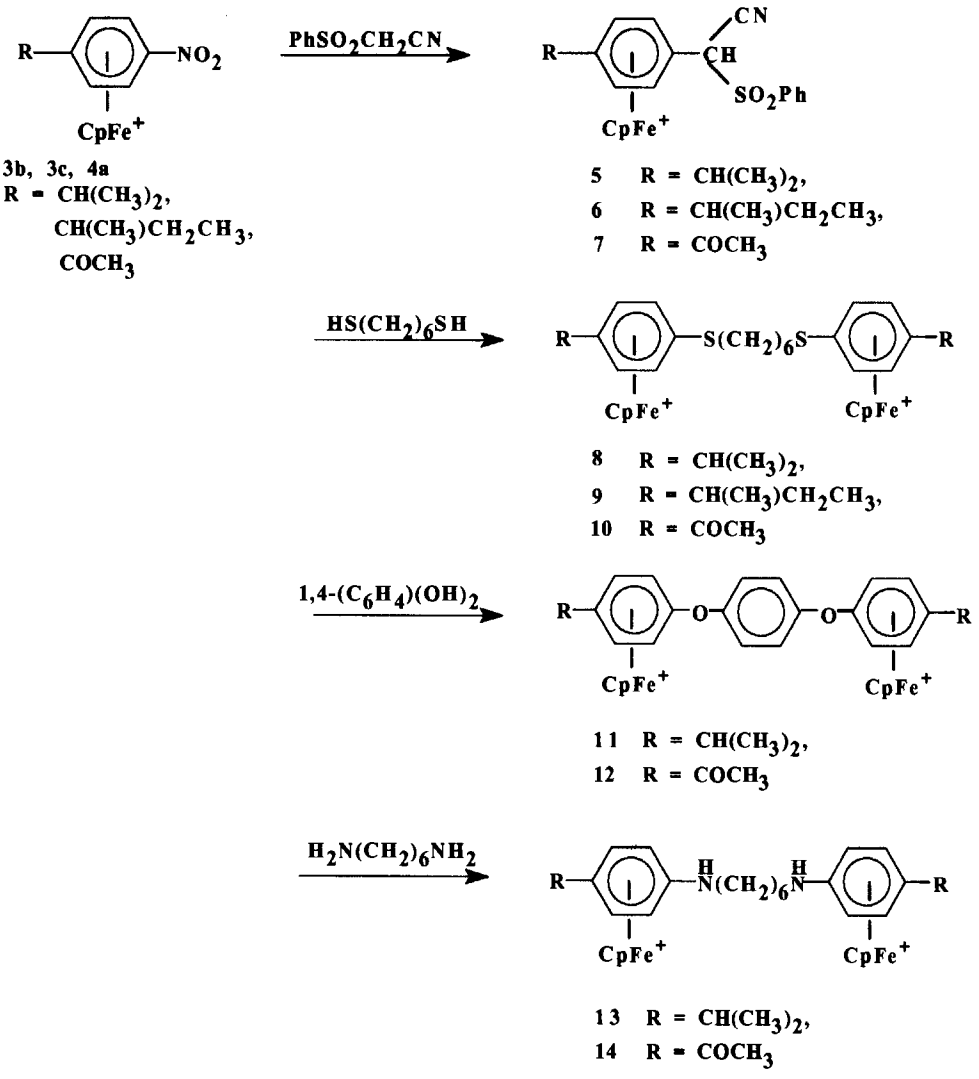
[a] A mixture of products was isolated and purified by crystallization to give **4a** and **4b**.

4a, as outlined in Table 1.† While oxidation of complex **2b** gave **3b** and **4a**, oxidation of the 4-sec-butylaniline complex led to the formation of the 4-sec-butylnitrobenzene complex **3c**, after 0.5 h and a mixture of two nitrobenzene complexes containing keto groups **4a** and **4b** after 24 h. Crystallization of this mixture led to the isolation of the two products in yields of 11 and 45%, respectively. The oxidation of 4-tert-butylaniline gave rise to only one product, **3d**, due to the lack of an α-methine group.

The synthesis of η^6-nitroarene-η^5-cyclopentadienyliron complexes extends the range of starting materials, which could be used in the preparation of compounds with biological applications or possible use in materials science.[1,5] Recently, we reported an efficient route to the synthesis of arylated phenylsulphonylacetonitriles using the cyclopentadienyliron moiety as an activating group.[6] As an example, complexes **3b, 3c** and **4a** reacted with phenylsulphonylacetonitrile to give complexes **5, 6** and **7** in 76–81% yield (Scheme 2).‡ This group of compounds are of interest to their potential use as precursors to alkanoic acids such as Ibuprofen.[7] The use of these nitroarene complexes in the synthesis of diiron complexes arises from our interest in the synthesis of bimetallic and polymetallic complexes with oxygen, sulphur and nitrogen bridges.[8–10] We have also reported the need for nitroarene complexes as starting materials in the nucleophilic substitution reactions with aromatic amines.[9,11] Preliminary results in the reactions of

† Satisfactory analytical data were obtained for all synthesized complexes. Selected data for new complexes. **3b**: ^{1}H NMR (200 MHz, CD_3COCD_3) 1.44 (d, $J = 6.96$ Hz, 6H, CH_3), 3.32 (septet, $J = 6.9$ Hz, 1H, CH), 5.44 (s, 5H, Cp), 6.86 (d, $J = 6.8$ Hz, 2H, complexed ArH), 7.52 (d, $J = 7.2$ Hz, complexed ArH); ^{13}C NMR (50.3 MHz, CD_3COCD_3) 23.00 (2C, CH_3), 33.43 (CH), 80.94 (5C, Cp), 84.65 (2C, complexed ArC), 87.06 (2C, complexed ArC), 111.79 (quaternary complexed ArC), 118.43 (quaternary complexed ArC). **4a**: ^{1}H NMR (CD_3COCD_3) 2.88 (s, 3H, CH_3), 5.54 (s, 5H, Cp), 7.42 (d, $J = 7.1$ Hz, 2H, complexed ArH), 7.75 (d, $J = 7.2$ Hz, 2H, complexed ArH); ^{13}C NMR (CD_3COCD_3) 27.36 (CH_3), 82.60 (5C, Cp), 85.81 (2C, complexed ArC), 88.79 (2C, complexed ArC), 97.00 (quarternary complexed ArC), 113.45 (quarternary complexed ArC), 197.78 (CO).

‡ NMR data for **5**: ^{1}H NMR (200 MHz, CD_3COCD_3) 1.44 (d, $J = 6.9$ Hz, 6H, CH_3), 3.29 (septet, $J = 6.9$ Hz, 1H, CH), 5.32 (s, 5H, Cp), 6.42 (d, $J = 6.7$ Hz, 2H, complexed ArH), 6.17–6.47 (m, 3H, complexed ArH and CH), 7.73–7.77 (m, 2H, SO_2Ph), 7.81–7.96 (m, 3H, SO_2Ph); ^{13}C NMR (50.3 MHz, CD_3COCD_3) 22.83 (CH_3), 22.98 (CH_3), 33.25 (CH), 61.56 (CH), 79.16 (5C, Cp), 86.69, 87.01, 87.26, 90.49 (4C, complexed ArC), 90.74 (quarternary complexed ArC), 113.06 (CN), 116.21 (quaternary complexed ArC), 130.67 (2C, SO_2Ph), 130.79 (2C, SO_2Ph), 134.93 (quarternary SO_2Ph), 137.20 (SO_2Ph).



Scheme 2.

complexes **3b, 3c** and **4a** leading to new bimetallic complexes containing alkyl or keto groups also proved to be successful, as described in Scheme 2.§

In conclusion, the discovery of the initial rapid oxidation followed by a second, slower oxidation of alkylated aniline complexes provided a new and wider range of nitroarene complexes which could be used as starting materials in the synthesis of various organic and organometallic compounds with potential biological activities as well as the use of these complexes as building blocks for larger organometallic systems.[5,6,8–10]

Acknowledgements—We thank NSERC (Canada), Manitoba Hydro and the University of Winnipeg for financial support. K.M.E. (graduate student, University of Manitoba) also thanks Mr J. Carneiro and Manitoba Hydro for assistance and a postgraduate scholarship. We would also like to thank Professor A. Piorko at St. Mary's University for discussion regarding the oxidation of the isopropylaniline complex.

§ NMR data for **10**: ^{1}H NMR (200 MHz, CD_3COCD_3) 1.59 (m, 4H, γ-CH_2), 1.82 (m, 4H, β-CH_2), 2.79 (s, 3H, CH_3), 3.37 (t, J = 7.2 Hz, 4H, α-CH_2), 5.22 (s, 10H, Cp), 6.76 (d, J = 6.8 Hz, 4H), 7.01 (d, J = 6.8 Hz, 4H); ^{13}C (50.3 MHz, CD_3COCD_3) 27.21 (1C, CH_3), 28.65 (2C, γ-CH_2), 28.75 (2C, β-CH_2), 31.95 (2C, α-CH_2), 80.25 (10C, Cp), 85.20 (4C, complexed ArC), 87.41 (4C, complexed ArC), 91.46 (2C, quaternary complexed ArC), 114.30 (2C, quaternary complexed ArC), 198.04 (2C, CO).

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