



## Synthesis and characterisation of new tricarbonyl (1-4-η - cyclohexa-1, 3-diene)-N- anilino iron complexes

T.I.Odiaka, I.A.Adejoro\*, O.F.Akinyele

Department of Chemistry, University of Ibadan, Ibadan, (NIGERIA)

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### ABSTRACT

X substituted anilines (X=3-NO<sub>2</sub>, 4-NO<sub>2</sub>, 2-Me, 3-Me and 4-Me) have been shown to act as nucleophiles to the organometallic cation [(Fe(CO)<sub>3</sub>(1-5-η - 2-MeOC<sub>6</sub>H<sub>6</sub>)] BF<sub>4</sub> and [(Fe(CO)<sub>3</sub>(1-5-η -C<sub>6</sub>H<sub>7</sub>)] BF<sub>4</sub>. This paper presents the nucleophilic addition of the substituted anilines to the dienyl ring of the organometallic complex to give new anilino-cyclohexa-1,3-diene iron tricarbonyl complexes. The reaction which takes place at room temperature gives Products which were isolated and characterized.

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### KEYWORDS

Anilino;  
Nitroanilino;  
Rotary Evaporation;  
Characterization and  
isolation.

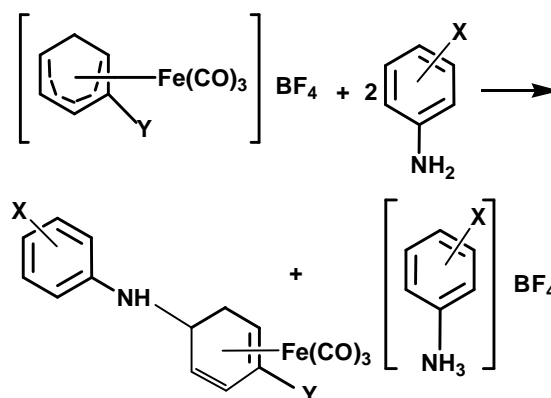
### INTRODUCTION

Organometallic cation [(Fe(CO)<sub>3</sub>(1-5-η -2-MeOC<sub>6</sub>H<sub>6</sub>)] BF<sub>4</sub> and [(Fe(CO)<sub>3</sub>(1-5-η -C<sub>6</sub>H<sub>7</sub>)] BF<sub>4</sub> have been reported in the literature<sup>[4,5]</sup>. The kinetics and mechanisms of these reactions has been a subject of extensive study of recent.<sup>[2-5,8-13]</sup>

The nucleophilic addition of these organometallics have lead the synthesis of novel organometallic compound of the type [C<sub>6</sub>H<sub>4</sub>NHX-C<sub>6</sub>H<sub>6</sub>Y (Fe(CO)<sub>3</sub>]<sup>[14-21]</sup> Y=H or 2-MeO.

This paper presents the synthesis and characterization of novel Tricarbonyl (1-4-η-5-exo-N-anilino-cyclohexa-1, 3-diene) iron. The Novel organometallics were synthesized by reacting anilines and selected aniline derivatives with [(1-5-η-C<sub>6</sub>H<sub>6</sub>Y) Fe(CO)<sub>3</sub>] BF<sub>4</sub> at room temperature to give XC<sub>6</sub>H<sub>4</sub>NH-C<sub>6</sub>H<sub>6</sub>Y Fe(CO)<sub>3</sub>. The reaction is represented in Scheme 1 below.

The complexes synthesized were characterized using micro analytical method, infra-red and <sup>1</sup>H.n.m.r.



Scheme 1

it was found that, they conform to those earlier reported in literature<sup>[1-10]</sup>. The implications of these synthetic route can not be over-stretched particularly when it born in mind that, organic or Natural product of interest could be synthesized using this route by treating the resulting organometallic with appropriate oxidizing agent such as trimethylamine oxide in benzene. Such Organics may be of immense medicinal value.

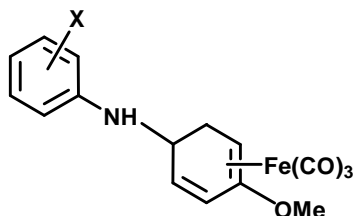
## EXPERIMENTAL

The Organometallic compound  $[(1-5-\eta-C_6H_6Y)(Fe(CO)_3)]BF_4$  ( $Y=H, 2MeO$ ) were synthesized using published procedure<sup>[1]</sup> and recrystallized from hot water. The anilines were purchased (BDH or Aldrich) in the purest grade available, the liquid sample were freshly distilled before use. Acetonitrile was distilled in bulk and magnesium sulphate added to remove traces of water before use. 0.15mmol of the  $[(1-5-\eta-C_6H_6Y)(Fe(CO)_3)]BF_4$  organometallic compound was dissolved in 5cm<sup>3</sup> of acetonitrile. 1.5mmol of the aniline and aniline derivatives were dissolved in 5cm<sup>3</sup> of acetonitrile, and all dissolutions were done at room temperature. The two solutions were mixed in 50ml beaker while stirring continuously.

The mixture was allowed to react at room temperature for 30 minutes. The mixture was shaken with 20cm<sup>3</sup> of diethylether /water (50/50: vol/vol) in separating funnel and ether layer transferred into a clean dried round bottom flask.

## PRODUCTS ISOLATION AND CHARACTERIZATION

Rotary evaporation of the ether extract under re-

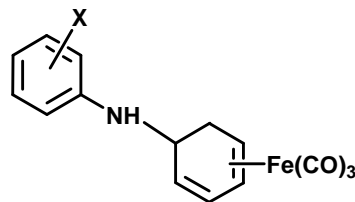


Scheme 2 : Structure of tricarbonyl (1-4-,  $\eta$ -5-Exo-N-anilino) 2- methoxycyclohexa-1, 3-diene iron complexes.

TABLE 1 : Nature of compound, infra-red spectra data and micro analytical data for tricarbonyl (1-4-,  $\eta$ -5-Exo-N-anilino) 2- methoxycyclohexa-1, 3-diene iron complexes

STRUCTURE	NATURE OF COMPOUND	I.R $\nu_{CO}$ $\nu_{(NH)cm^{-1}}$	MICROANALYSIS Found (Calculated)	
			C	H
3-NO <sub>2</sub>	Orange crystalline solid	2045,1970 (3450)	50.36 (50.6)	3.51 (3.40)
4-NO <sub>2</sub>	Orange crystalline solid	2045,1970 (3450)	50.35 (50.6)	3.45 (3.40)
2-Me	Brown oil	2045,1970 (3450)	59.31 (59.1)	4.63 (4.65)
3-Me	Brown oil	2045,1970 (3450)	58.70 (59.1)	4.70 (4.65)
4-Me	Brown oil	2045,1970 (3450)	59.40 (59.1)	4.50 (4.65)

duced pressure afforded orange crystalline solid / brown oil in good yield. Details of the infra-red spectrum in potassium bromide disc, microanalytical measurement and proton nuclear magnetic resonance spectroscopy are shown in the TABLE below.



Scheme 3 : Structure of tricarbonyl (1-4-  $\eta$ -5-Exo-N-anilino) cyclohexa-1, 3-diene iron complexes

TABLE 2 : Nature of compound, infra-red spectra data and micro analytical data for tricarbonyl (1-4-  $\eta$ -5-Exo-N-anilino) cyclohexa-1, 3-diene iron complexes

STRUCTURE	NATURE OF COMPOUND	I.R $\nu_{CO}$ $\nu_{(NH)cm^{-1}}$	MICROANALYSIS Found (Calculated)	
			C	H
3-NO <sub>2</sub>	Orange solid	2045,1970 (3450)	48.6 (48.1)	3.95 (3.74)
4-NO <sub>2</sub>	Yellow solid	2045,1970 (3450)	47.9 (48.1)	3.87 (3.74)
2-Me	Brown oil	2045,1970 (3450)	46.2 (45.5)	5.34 (4.96)
3-Me	Brown oil	2045,1970 (3450)	44.94 (45.5)	5.08 (4.96)
4-Me	Brown oil	2045,1970 (3450)	45.86 (45.5)	5.16 (4.96)

TABLE 3 : <sup>1</sup>H.n.m.r spectra data for new tricarbonyl (1, 4- $\eta$ -5-Exo-N anilino) 2-methoxycyclohexa-1, 3-diene iron complexes in D<sub>6</sub>-acetone.

X	PROTONS	CHEMICAL SHIFT	RELATIVE INTENSITY	MULTIPLICITY
3-NO <sub>2</sub>	H <sup>1,4</sup>	7.20	2	m
	H <sup>3</sup>	5.05	1	m
	H <sup>5*</sup>	5.20	1	m
	H <sup>6*</sup>	7.60	1	m
	H <sup>6</sup>	8.10	1	m
	CH <sub>3</sub>	6.80	3	s
	Har	3.0-3.70		
4-NO <sub>2</sub>	H <sup>1,4</sup>	7.20	2	m
	H <sup>3</sup>	5.00	1	m
	H <sup>5*</sup>	5.15	1	m
	H <sup>6</sup>	8.70	1	m
	H <sup>6*</sup>	8.55	1	m
	OCH <sub>3</sub>	6.80	3	s
	Aromatic protons	2.60 3.80	2 2	d m

Continued

## Full Paper

X	PROTONS	CHEMICAL SHIFT	RELATIVE INTENSITY	MULTIPLICITY
2-Me in d <sub>3</sub> Acetonitrile	H <sup>1,4</sup>	7.15	2	m
	H <sup>3</sup>	5.05	1	m
	H <sup>5</sup>	5.30	1	m
	H <sup>6<sup>o</sup></sup>	7.80	1	m
	H <sup>6</sup>	8.25	1	m
	OCH <sub>3</sub>	6.85	3	s
	CH <sub>3</sub>	8.40	3	s
	Har	3.30-4.10	2	m
3-Me	N-H	6.0	1	b
	H <sup>1,4</sup>	7.20	2	m
	H <sup>3</sup>	5.06	1	m
	H <sup>5</sup>	5.19	1	m
	H <sup>6</sup>	7.50	1	m
	H <sup>6<sup>o</sup></sup>	8.20	1	m
	OCH <sub>3</sub>	6.74	3	s
	CH <sub>3</sub>	8.32	3	s
	Har	3.48	1	s
	Har	3.62	1	t
4-Me	Har	4.15	2	d
	N-H	5.90	1	b
	H <sup>1,4</sup>	6.85	2	m
	H <sup>3</sup>	4.30	1	m
	H <sup>5<sup>o</sup></sup>	4.90	1	m
	H <sup>6<sup>o</sup></sup>	7.40	1	m
	H <sup>6</sup>	8.30	1	m
	OCH <sub>3</sub>	6.20	3	s
Aromatic protons	CH <sub>3</sub>	7.45	3	s
		1.60	2	d
		2.50	2	d
	N-H	5.60	1	b

## RESULTS AND DISCUSSION

The products isolated from the reactions of complex (Scheme 2) with 3-nitroaniline, 4-nitroaniline, 2-methylaniline, 3-methylaniline and 4-methylaniline are all air stable yellow solid/ yellow oils. Their I.r spectra were run in KBr disc within the range 2500 and 800cm<sup>-1</sup>. These products showed intense and sharp V (co) bands in acetonitrile at 2045 and 1970cm<sup>-1</sup> as well as abroad and weak (V<sub>NH</sub>) band in nujol mull at ca 3400cm<sup>-1</sup>. Their stability in air allowed further characterization of all the products by <sup>1</sup>H.n.m.r spectroscopy.

Their <sup>1</sup>H.n.m.r spectra as well as the position of the I.r. V(co) bands are characteristic of tricarbonyl (1-4- $\eta$ -5-exo-N-anilino-2-methoxycyclohexa-1,3-diene)iron derivatives, these features are very similar to those reported for a wide variety 1,3-diene-aniline derivatives involving exo-addition at the diene ring of organometallics of type in Scheme 2, for example the <sup>1</sup>H.n.m.r spectrum of 3-methylanilino complex in d<sub>6</sub>-acetone showed overlapping multiplets characteristic of the inner (H<sup>3</sup>) and the outer (H<sup>1</sup> and H<sup>4</sup>) -diene protons at 5.06 $\tau$  and 7.20 $\tau$  respectively. The H<sup>6</sup> (endo) and H<sup>6</sup> (exo) methylene protons appear at 7.50 $\tau$  and 8.20 $\tau$  while the H<sup>5</sup> (endo) proton adjacent to the N-methylanilino is shifted down field to 5.19 $\tau$ . The broad resonance at Ca 5.90 $\tau$  is assigned to the -NH proton since addition D<sub>2</sub>O (deuterium Oxide) lead to the disappearance of this signal indicating the replacement of hydrogen with deuterium to form -ND in the complex. The multiplet at 3.48 $\tau$ , triplet at 3.62 $\tau$  and doublet (intensity of 2) at 4.15 $\tau$  are all assigned to the aromatic protons.

The singlet (intensity of 3 in each case) at 6.74 $\tau$  and 8.32 are assigned to the OCH<sub>3</sub> and CH<sub>3</sub> protons respectively. The above assignments unequivocally confirm the structure of 3-methylanilino (Cyclohexa-1,3-diene) iron tricarbonyl. Similar features were clearly demonstrated by other products.

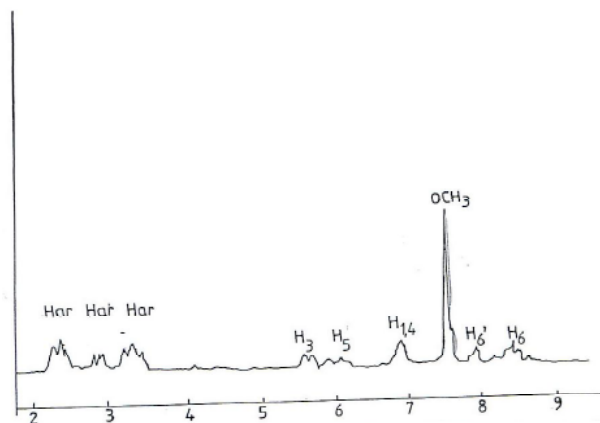
The <sup>1</sup>H.n.m.r. spectra of the 3-nitroanilino and 2-methylanilino derivatives are reproduced in Figures 1 and 2, the microanalytical measurements carried out for these 1,3-diene-anilino products are shown in TABLE 1 and 2.

## CONCLUSION

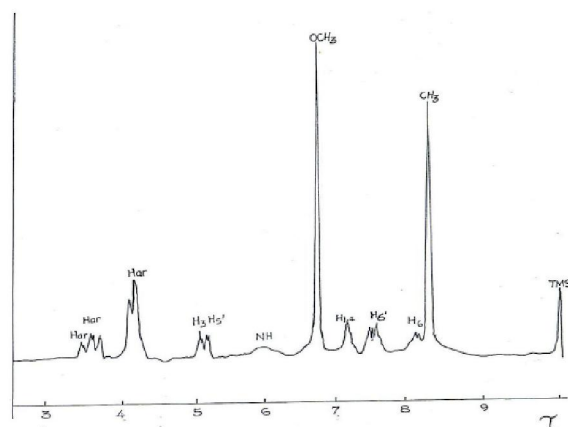
We have succeeded in synthesizing ten new organometallics resulting from the addition of anilines to the complexes (1-5- $\eta$ -dienyl) BF<sub>4</sub>. Dienyl=C<sub>6</sub>H<sub>7</sub> or 2-MeOC<sub>6</sub>H<sub>6</sub> in acetonitrile.

This work has clearly demonstrated the application of organometallic to the synthesis of novel co-ordinated organics and the ease (room temperature and pressure) with which the products could be prepared. The synthetic utility of these reactions cannot be over-emphasized here particularly when it is borne in mind that careful treatment of these products with appropriate oxidizing

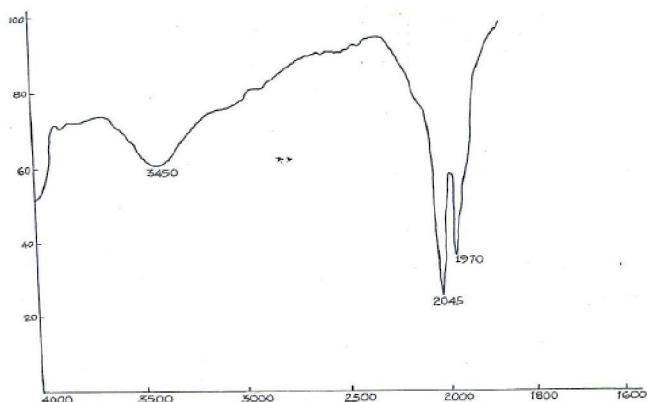
agent such as  $\text{Me}_3\text{NO}$  in benzene leads to the cleavage of the iron tricarbonyl unit, thus affording novel 1,3-diene substituted organics. Careful selection of reacting nucleophiles such as  $\beta$ -carbolines<sup>[22,23]</sup> or other natural products of interest would no doubt afford new drugs of medicinal interest.



**Figure 1 : Proton n.m.r. spectrum of 1,4- $\eta$ -2 methoxy cyclohexa-1,3-diene, 3-nitroanilino iron tricarbonyl.**



**Figure 2 : Proton n.m.r. spectrum of 1,4- $\eta$ -2-methoxy cyclohexa-1-3-diene-3-methylanilino iron tricarbonyl**



**Figure 3 : Infra-red spectrum of 1,4- $\eta$ -2 methoxy cyclohexa-1-3-diene, 3-nitroanilino iron tricarbonyl.**

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