Synthesis and Characterization of Pyridino(1,4-*H*-cyclohexa-1,3-diene) Derivatives of Iron Tricarbonyl Complexes

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Abstract: In this synthesis, we have been able to show that, the addition of *x*-substituted pyridines, (*X* = H, 2- Me, 3- Me 4- Me, 4-NH₂ and 4-N(CH₃)₂) to the dienyl ring of the organometallic cation, [(Fe(CO)₃ (1-5- η -2-MeOC₆H₆)]BF₄ and [(Fe(CO)₃ (1-5- η -C₆H₇)]BF₄ gives ionic substituted diene products, (X C₅H₄-C₆H₆Y (Fe(CO)₃] BF₄, Y=H or 2-MeO. The reaction takes place at ordinary room temperature. The resulting products were isolated and characterized.

Keywords: Pyridino, Methylpyridino, Exo-substituted, Isolation, methoxycyclohexa-1, 3-Diene

Introduction

The organometallic complex of the type [(Fe(CO)₃ (1-5- η -C₆H₆Y)]BF₄ have been widely reported in the literature as electrophiles to a wide varieties of organic substrates and the kinetics of these reactions have been a subject of intense study¹⁻¹⁰. The additions of these organometallics have led to the discovery of novel 1, 3-diene substituted iron tricarbonyl products in good yield¹¹⁻²⁰. The iron tricarbonyl moiety in these products may be readily cleaved²⁰⁻²² by using oxidizing agents such as Me₃NO thus affording organic derivatives which are inaccessible by conventional organic synthetic routes.

In this paper, we present the syntheses and characterizations of these novel pyridine-(1, 4- η - cyclohexa-1, 3-diene) derivatives of iron tricarbonyl. The reactions between pyridine and selected pyridines with the organometallic complex of the type [Fe (CO)₃ (1-5- η -C₆H₆Y)]BF₄ (Y=H or 2-MeO), at room temperature is represented as shown in Scheme 1.

Scheme 1

Experimental

The organometallic compound $[(\text{Fe}(\text{CO})_3(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_6\text{Y}))]\text{BF}_4$ was synthesized and purified by published procedure¹ and was crystallized from hot water. The pyridine/ pyridines derivatives were purchased (BDH or Aldrich) in the purest grade available. The liquid samples were freshly distilled before use. Acetonitrile (Solvent) was distilled in bulk and magnesium sulphate added to remove traces of water before use. 0.15 mmol of the organometallic complex was dissolved in 5 cm³ of acetonitrile, 1.5 mmol of the nucleophiles, each dissolved in 5 cm³ of acetonitrile and all dissolutions were done at room temperature. The two solutions were mixed in 50 mL beaker while stirring continuously. The mixtures were allowed to stand at room temperature for 10 minutes.

Products isolation and characterization

Rotary evaporation of each mixture at 35 °C and at reduced pressure produced brown solids which were shaken and washed with 20 cm³ of light petroleum spirit (60-80 °C) and filtered. The resulting products were washed several times with petroleum ether to remove excess pyridines and dried to give $[(\text{Fe}(\text{CO})_3\text{C}_6\text{H}_6\text{Y-C}_5\text{H}_4\text{X})]^+$ as itemized below (Scheme 2 & 3). Details of the infra-red spectrum in potassium bromide disc, micro-analytical measurement and proton nuclear magnetic resonance spectroscopy are shown in the Table 1, 2 and 3 respectively.

Scheme 2. Structure of new pyridino(1,4- η -2-methoxycyclohexa-1,3-diene) derivatives of iron tricarbonyl complexes

Table 1. Nature of compound, infra-red spectra data and micro analytical data for the (1, 4- η 2-methoxycyclohexa- 1-3-diene -5-exo-*N*-pyridino derivatives of iron tricarbonyl complexes

Structure X		Nature of Compound	IR ν_{CO} (ν_{BF_4})cm ⁻¹	Microanalysis Found (Calculated),%	
				C	H
I	H	Pale yellow solid	1980, 2055 (1060)	43.46 (43.6)	3.15 (3.2)
II	2-Me	Brown Oil	1980, 2055 (1060)	44.83 (45.1)	3.62 (3.55)
III	3-Me	Brown Oil	1980,2055 (1060)	44.96 (45.1)	3.52 (3.55)
IV	4-Me	Brown Oil	1980,2055 (1060)	44.96 (45.1)	3.52 (3.55)
V	4-NH ₂	Brown solid	1980,2055 (1060)	42.7 (42.0)	3.32 (3.27)
VI	4-N(CH ₃) ₂	Brown solid	1980,2055 (1060)	44.49 (44.9)	3.95 (4.00)

Table 2. Nature of compound, infra-red spectra data and micro analytical data for the (1,4- η - cyclohexa-1-3-diene -5-exo-*N*-pyridino derivatives of iron tricarbonyl complexes

Structure X		Nature of compound	IRvco (ν_{BF_4}) cm^{-1}	Microanalysis Found (Calculated),%	
				C	H
I	H	Yellow solid	1980,2055 (1060)	54.1 (54.9)	4.2 (4.3)
II	2-Me	Brown oil	1980,2055 (1060)	55.8 (56.14)	4.4 (4.7)
III	3-Me	Brown oil	1980,2055 (1060)	54.9 (56.14)	4.3 (4.7)
IV	4-Me	Brown oil	1980,2055 (1060)	55.1 (56.14)	4.5 (4.7)
V	4-NH ₂	Brown solid	1980,2055 (1060)	51.95 (52.23)	4.8 (4.65)
VI	4-N(CH ₃) ₂	Brown solid	1980,2055 (1060)	55.1 (54.84)	5.51 (5.38)

Table 3. ¹H-NMR spectra data for the tricarbonyl 1,4- η -5-exo-(*N*-pyridino derivatives) 2- methoxycyclohexa-1,3-diene iron complexes

X	Protons	Chemical shift, δ	Relative intensity	Multiplicity
H	H ^{1,4}	6.90	2	m
	H ³	5.60	1	m
	H ⁵ ,	5.90	1	m
	H ⁶ ,	7.90	1	m
	H ⁶	8.40	1	m
	CH ₃	7.57	3	s
	Aromatic protons	2.30	2	t
		2.90	1	t
		3.30	2	t
2-Me	H ^{1,4}	6.95	2	m
	H ³	5.50	1	m
	H ⁵ ,	5.95	1	m
	H ⁶	8.00	1	m
	H ⁶	8.30	1	m
	OCH ₃	6.70	3	s
	CH ₃	7.50	3	s
	Aromatic protons	2.70	2	t
		3.10	1	t
		3.5	1	t
3-Me	H ³	1.90	1	m
	H ⁵	5.10	1	m
	H ⁶	7.10	1	m
	H ⁶ ,	8.40	1	m
	OCH ₃	6.70	3	s
	CH ₃	6.30	3	s
	Aromatic protons	2.40-3.55	2	d
			2	d

Contd...

4-Me <i>In situ</i> d ₃ Acetonitrile	H ^{1,4}	6.85	2	m
	H ³	4.30	1	m
	H ⁵	4.90	1	m
	H ⁶	7.40	1	m
	H ⁶	8.30	1	m
	OCH ₃	6.20	3	s
	CH ₃	7.45	3	s
	Aromatic protons	1.49	2	d
		2.30	2	d
4-NH ₂	H ^{1,4}	6.80	2	m
	H ³	4.40	1	m
	H ⁵	5.10	1	m
	H ⁶	7.60	1	m
	H ⁶	8.50	1	m
	OCH ₃	6.60	3	s
	CH ₃	7.50	3	s
	Aromatic protons	1.60	2	d
4-N(CH ₃) ₂	H ^{1,4}	6.90	2	m
	H ³	5.50	1	m
	H ⁵	5.40	1	m
	H ⁶	7.70	1	m
	H ⁶	8.60	1	m
	OCH ₃	6.80	3	s
	CH ₃	7.40	3	s
	Aromatic protons	1.60	2	d
		2.50	2	d

Scheme 3. Structure of new pyridino(1,4- η -cyclohexa-1,3-diene) derivatives of iron tricarbonyl complexes

Results and Discussion

The reaction of complex with pyridine/pyridine derivatives ($X=H, 2\text{-Me}, 3\text{-Me}, 4\text{-Me}, 4\text{-NH}_2$ and $4\text{-N}(\text{CH}_3)_2$) showed intense sharp $\nu(\text{co})$ bands (in acetonitrile) at 2055 and 1980 cm^{-1} as well as a broad band (nujol mull) due to the tetrafluoroborate anion at ca 1060 cm^{-1} in their IR spectra. Product 1 was isolated as a pale yellow crystalline, air-stable solid, fully characterized by IR, ^1H NMR and microanalytical measurements. Its ^1H NMR spectrum is shown in Figure 2. This clearly demonstrates that, the products are tricarbonyl (1,4- η -5 *exo-N*-pyridino 2-methoxycyclohexa-1,3-diene iron tetrafluoroborate. The features shown in this spectrum (Figures 1 and 2) together with $\nu(\text{co})$, IR bands at 2055 and 1980 cm^{-1} in Figure 3 have been reported as characteristic features^{23,24}.

Figure 1. ¹H NMR spectrum of 1,4- η -2-methoxycyclohexa-1-3-diene-*N*-pyridino iron tricarbonyl

Figure 2. ¹H NMR spectrum of 1,4- η -2-methoxycyclohexa-1-3-diene-*N*-2 methylpyridino iron tricarbonyl

Figure 3. IR spectrum of 1,4- η -2-methoxycyclohexa-1-3-diene-*N*-pyridino iron tricarbonyl

Conclusion

We have succeeded in synthesizing twelve new organometallics resulting from the nucleophilic addition of pyridine/pyridine derivatives to the organometallic compound $[(\text{Fe}(\text{CO})_3(1,5\text{-}\eta\text{-2-MeOC}_6\text{H}_6)]\text{BF}_4$ and $[(\text{Fe}(\text{CO})_3(1,5\text{-}\eta\text{-C}_6\text{H}_7)]\text{BF}_4$ in acetonitrile. This work has clearly demonstrated the application of organometallic to the synthesis of novel coordinated organics and the ease with which these products could be prepared.

The synthetic utility of these complexes cannot be over-emphasized here, particularly when it is born in mind that careful treatment of the products with oxidizing agents such as Trimethylamine oxide in benzene leads to the cleavage of the Iron tricarbonyl, thus affording a novel 1,3-diene substituted organics.

References

1. Birch A J, Cross P E, Lewis J, White D A and Wild S B, *J Chem Soc (A)*, 1968, 332-346.
2. Odiaka T I and Williams P.A, *J Chem Soc Dalton Trans.*, 1981, 200-204.
3. Odiaka T I and Kane-Macguire L A P, *J Chem Soc Dalton Trans.*, 1981, 1162-1168.
4. Odiaka T I, Kane-Maguire L A P, Turgoose S and Williams P A, *J Organomet Chem.*, 1980, **188**, C5-C9.
5. Odiaka T I, Kane-Maguire L A P, Turgoose S and Williams P A, *J Chem Soc Dalton Trans.*, 1981, 2489-2495.
6. Brian F G, Johnson J, Ian E Ryder and Martyn V Tivigg, *J Chem Soc Dalton Trans.*, 1976, 421-425.
7. Odiaka T I, Ph. D Thesis, University of Wales, Cardiff, U.K, 1980.
8. Odiaka T I and Kane-Maguire, *J Organomet Chem.*, 1985, **284**, 35-36.
9. Odiaka T I, *Org Chim Acta*, 1985, **103**, 9-13.
10. Odiaka T I, *J Organomet Chem.*, 1987, **321**, 227-235.
11. Odiaka T I, *Organic Chim Acta*, 1988, **145**, 267-271.
12. Odiaka T I, *J Organomet Chem.*, 1988, **345**, 135- 141.
13. Odiaka T I and Okogun J.I, *J Organomet Chem.*, 1985, 288, C30-C32.
14. Birch A J and Williamson D H, *J Chem Soc Perkin Trans 2*, 1973, 1892-1900.
15. Keally T J and Pauson P L, *Nature*, 1951, **168**, 1039-1044.
16. McCleverty J.A, *J Organomet Chem Rev.*, 1976, **119**, 261.
17. Criad A Poffenberger, Norman H Tennent and Andrew Wojcicki, *J Organomet Chem.*, 1980, **127**, 193-196.
18. Shvo V Belsky and Dodsik H, *J Chem Soc Chem Comm.*, 1974, 336-340.
19. Pearson A J and Rees D C, *Tetrahedron Lett.*, 1980, **21**, 8927-8943.
20. Pearson A J, Academic press, ISBN 0-12-548270, 1994.
21. Hegedus L S, University Science Books ISBN 0-935702-28-8, 1994.
22. Odiaka T I, Okogun J I and Okorie D O, *J Sci Res.*, 2007, **7(1)**, 1-8.
23. Comely A C, Gibson S E, Hales N J and Peplow M A, *J Chem Soc Perkin Trans I*, 2002, 2526-2531.
24. Dinh L V, Hampel F and Gladysz J.A, *J Organomet Chem.*, 2005, **690**, 493-503.