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THE SYNTHESIS AND CHARACTERIZATION OF TRICARBONYLCHROMIUM COMPLEXES OF SUBSTITUTED ANILINES AND FLUOROBENZENES

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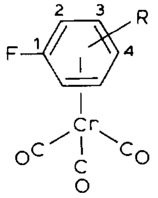
Summary

The tricarbonylchromium complexes of the *o*, *m* and *p* isomers of the following arenes were prepared: fluorotoluene, fluoroanisole, fluoroaniline and anisidine together with the complexes of 1-fluoro-2,3-dimethylbenzene, 5-fluoro-2-methylaniline and methyl anthranilate. Preparative and spectral information is presented.

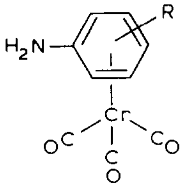
In 1978 we reported [1] an efficient preparative technique for arenetricarbonylchromium complexes. It achieves high conversions in relatively short reaction times by the addition of a small percentage (generally about 20%) of tetrahydrofuran to the principal solvent, di-n-butyl ether. As well as washing back the subliming hexacarbonylchromium, the tetrahydrofuran apparently has a specific catalytic effect on the reaction of this carbonyl with arenes, perhaps by forming an unstable intermediate complex $(THF)_nCr(CO)_{6-n}$.

Since 1978 both ourselves [2] and a number of other workers have reported using the method successfully to make a wide variety of tricarbonylchromium complexes [3–5].

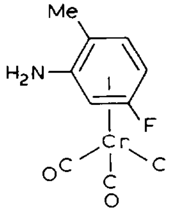
In the present paper the utility of the method in producing complexes which are derivatives of anilinetricarbonylchromium and fluorobenzenetricarbonylchromium is illustrated. Some of the compounds synthesized have been made before but many have been reported without spectral or microanalytical data. Complex Ia has been fully reported by a number of workers [6,7] and is included only for comparison. Complexes Ib, Ic, Ih and Ij have been reported [8] without spectral or microanalytical data. Complexes IIb, IIc and IId have similarly been reported [9]. Complexes Id, Ie, If, Ig, Ii, IIa and III are new compounds. Utilizing this method the synthesis of these complexes is relatively straightforward, however, several possible problems should be noted. For complexes where the free arene has a boiling point < 150°C an excess of the arene may be used as it can be removed with the solvents at the end of the reaction. If, however, the boiling point of the free arene is such that it may not



(Ia, R = 4-Me,
Ib, R = 3-Me,
Ic, R = 2-Me,
Id, R = 4-MeO,
Ie, R = 3-MeO,
If, R = 2-MeO,
Ig, R = 2,3-Me,
Ih, R = 4-NH_2,
Ii, R = 3-NH_2,
Ij, R = 2-NH_2)



(IIa, R = 4-MeO,
IIb, R = 3-MeO,
IIc, R = 2-MeO,
IId, R = 2-CO_2Me)



(III)

be removed using a rotary evaporator then a slight excess of the $Cr(CO)_6$ should be used (see Table 1).

Further, the complexes containing NH_2 groups (especially IIb, IIc and III) are extremely light sensitive whilst in solution during the workup procedure. After the initial solvent removal it is necessary to use flasks and other glassware which have been covered with aluminium foil. These complexes are, however, not unusually sensitive to light after they have been obtained in the solid form. All of the complexes are yellow except IId which is orange-red. ^1H NMR data for complexes Ia–Ij, IIa–IId and III are reported in Table 2. The complexes IIa–IId are rather insoluble in chloroform and therefore were run in acetone-d_6.

Experimental

All reactions were conducted in an atmosphere of nitrogen. Light petroleum refers to the fraction b.p. 40–60°C. All arenes were purchased from Aldrich Chemical Co. and used as received. A typical procedure is described below; other experimental data are collected in the tables. All melting points were performed in sealed, evacuated capillaries.

2-Fluorotoluenetricarbonylchromium

Hexacarbonylchromium (4.0 g, 18.2 mmol) and 2-fluorotoluene (10.0 g, 90.8 mmol) were heated under reflux in a mixture of di-n-butyl ether (100 cm^3) and tetrahydrofuran (20 cm^3) for 42 h. The cooled solution was then filtered and the solvents evaporated under reduced pressure. The residue was dissolved in ether, refiltered and the product precipitated by the addition of light petroleum. Some additional solvent removal may be necessary to aid precipitation.

Recrystallization from ether/light petroleum gave 2-fluorotoluenetricarbonylchromium (2.7 g, 61%). Other details are given in Table 1.

TABLE 1. REACTIONS OF ARENES WITH 4 g (18.2 mmol) OF $Cr(CO)_6$ TO GIVE THE CORRESPONDING COMPLEXES (η^6-arene)$Cr(CO)_3$

Complex	Arene		Reflux time (h)	Yield [a]		Product m.p. (°C)	Microanalysis (Found (calcd.) (%))		
	g	mmol		g	%		C	H	N
Ia	3.0	27.2	42	2.3	52	61–62 [b]	Lit. [8]		
Ib	5.9	54.0	42	2.2	49	68–69 [c]	49.0	3.0	
							(48.8)	(2.9)	
Ic	10.0	90.8	42	2.7	61	73–74	48.7	2.85	
							(48.8)	(2.9)	
Id	4.2	33.6	42	2.2	46	69–70	46.0	2.6	
							(45.8)	(2.7)	
Ie	2.8	21.9	42	1.4	50	62–64	46.1	2.7	
							(45.8)	(2.7)	
If	3.4	26.7	42	2.4	51	91–93	45.6	2.7	
							(45.8)	(2.7)	
Ig	2.0	16.0	42	1.5	36	69–71	50.4	3.45	
							(50.8)	(3.5)	
Ih	1.8	15.8	27	2.1	52	104–106 [d]	43.4	2.4	5.4
							(43.7)	(2.45)	(5.7)
Ii	1.4	12.5	19	1.4	50	139–141	43.7	2.4	5.5
							(43.7)	(2.45)	(5.7)
Ij	1.4	12.5	27	2.0	64	138–140 [e]	43.8	2.4	5.5
							(43.7)	(2.45)	(5.7)
IIa	1.0	8.1	21	1.9	90	109–110	46.1	3.5	5.2
							(46.3)	(3.5)	(5.4)
IIb	1.1	8.9	21	1.8	78	157–158 [f]	46.2	3.5	5.3
							(46.3)	(3.5)	(5.4)
IIc	1.3	10.6	21	2.0	73	124–126 [g]	46.1	3.5	5.2
							(46.3)	(3.5)	(5.4)
IId	1.2	7.8	21	1.6	70	209–210 [h]	46.0	3.2	4.9
							(46.0)	(3.2)	(4.9)
III	0.9	7.2	21	1.4	71	104–106	45.6	3.1	5.2
							(46.0)	(3.1)	(5.4)

[a] Reported yields are for complexes that have been recrystallized once from the crude product. [b] Lit. [8] 59–60°C. [c] Lit. [10] 63°C. [d] Lit. [8] 102°C. [e] Lit. [8] 138°C. [f] Lit. [9] 160°C. [g] Lit. [9] 127°C. [h] Lit. [9] 198°C.

TABLE 2

IR (ν(CO) in C_6H_{12} [a]) AND NMR SPECTRA (δ from TMS in $CDCl_3$ [b]) FOR COMPLEXES I–III

Complex	IR (cm^{-1})	^1H NMR	
		Complexed ring	Other protons
Ia	1957, 1898, 1886	5.35 A_2B_2 pattern	2.07 (3H, s, *p*-Me)
Ib	1957, 1893, 1887	4.69–4.82 (1H, br d) 5.15–5.35 (2H, m) 5.40–5.63 (1H, m)	2.26 (3H, s, *m*-Me)
Ic	1956, 1889	4.85–5.60 (1H, m) 5.25–5.7 (3H, m)	2.25 (3H, d, *o*-CH_3, $J \sim 1$ Hz F coupling
Id	1954, 1887	5.15–5.30 (2H, m) 5.49–5.65 (2H, m)	3.62 (3H, s, *p*-MeO)
Ie	1956, 1889, 1885	4.75–4.90 (1H, m) 4.97–5.16 (1H, m) 5.29–5.42 (1H, m) 5.46–5.66 (1H, m)	3.76 (3H, s, *m*-MeO)
If	1955, 1886	4.95–5.2 (2H, m) 5.25–5.4 (1H, m) 5.54–5.7 (1H, m)	3.85 (3H, s, *o*-MeO)
Ig	1950, 1887, 1879	4.78–4.92 (1H, br m) 5.28–5.43 (2H, m)	2.20 (3H, d, CH_3 *ortho* to F, $J \sim 1$ Hz F coupling) 2.28 (3H, s, CH_3 *meta* to F)
Ih	1973, 1967, 1901, 1890	4.73–4.96 (2H, m) 5.50–5.70 (2H, m)	3.40 (2H, br s, NH_2)
Ii	1968, 1899, 1891	4.40–4.60 (1H, m) 4.90–5.18 (2H, m) 5.40–5.19 (1H, m)	3.64 (2H, br s, NH_2)
Ij	1952, 1965, 1897, 1888	4.71–4.95 (1H, m) 5.03–5.29 (2H, m) 5.65–5.81 (1H, m)	3.72 (2H, br s, NH_2)
IIa	1955, 1950, 1873	5.39 A_2B_2 pattern	3.61 (3H, s, *p*-MeO) 3.81 (2H, br s, NH_2)
IIb	1955, 1949, 1873	4.75–5.00 (2H, m) 5.18–5.24 (1H, m) 5.67–5.82 (1H, m)	3.71 (3H, s, *m*-MeO) 4.25 (2H, v. br s, NH_2)
IIc	1953, 1881, 1870	4.96–5.06 (1H, m) 5.30–5.40 (2H, m) 5.75–5.83 (1H, m)	3.81 (3H, s, *o*-MeO) 3.9 (2H, v br, s, NH_2) (*o*-MeO and NH_2 peaks superimposed on each other)
IId	1965, 1962, 1881	4.95–5.30 (2H, m) 5.88–6.10 (1H, m) 6.30–6.41 (1H, m)	3.87 (3H, s, Me) 6.45 (2H, v br s, NH_2) (Superimposed on 6.30–6.41 complexed ring peak)
III	1963, 1895, 1881	4.90–5.25 (2H, m) 5.5–5.66 (1H, m)	2.00 (3H, s, Me) 3.75 (2H, br s, NH_2)

[a] Complexes IIa and IId were run in $C_6H_{12}/CDCl_3$ 50/1. [b] Spectra IIa–IId run in acetone-d_6.

The other compounds in Table 1 were prepared and purified similarly except that compounds IIa–IId were recrystallized from acetone/light petroleum. Microanalytical samples were prepared by a further recrystallization.

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