

ARENE TRANSITION METAL COMPLEXES IN REACTIONS WITH NUCLEOPHILIC AGENTS



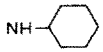
XII *. THE SYNTHESIS OF A SERIES OF BIS(ARENE)CHROMIUM COMPLEXES WITH A VARIED SUBSTITUENT IN ONE OF THE LIGANDS

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Summary

An approach to the synthesis of a series of bis(arene)chromium complexes with a varied substituent in one of the ligands has been worked out, which involves low-temperature co-condensation of chromium vapours with arenes followed by the modification of substituents in arene ligands. In this way a series of complexes have been obtained: $(\eta\text{-C}_6\text{H}_5\text{Cl})(\eta\text{-C}_6\text{H}_5\text{X})\text{Cr}^+\text{A}^-$ ($\text{X} = \text{H}$, NMe_2 , , , , OMe , OEt , OPr-i , OBu-n , Cl , CO_2H , CO_2Me , CF_3); $(\eta\text{-C}_6\text{H}_6)(\eta\text{-XC}_6\text{H}_4\text{Cl})\text{Cr}^+\text{A}^-$ ($\text{X} = \text{H}$, $p\text{-NMe}_2$, $p\text{-OMe}$, $m\text{-OMe}$, $p\text{-Me}$, $m\text{-Me}$, $p\text{-Cl}$, $m\text{-Cl}$, $p\text{-CO}_2\text{Me}$, $m\text{-CO}_2\text{Me}$, $p\text{-CO}_2\text{H}$, $m\text{-CO}_2\text{H}$) ($\text{A}^- = \text{PF}_6^-$, BPh_4^-); $(\eta\text{-C}_6\text{H}_5\text{X})(\eta\text{-C}_6\text{H}_5\text{CO}_2\text{H})\text{Cr}^+\text{PF}_6^-$ ($\text{X} = \text{H}$, OPr-i , OBu-n , OMe , Me , Cl , CO_2H , CO_2Me , CF_3); $(\eta\text{-C}_6\text{H}_6)(\eta\text{-XC}_6\text{H}_4\text{CO}_2\text{H})\text{Cr}^+\text{PF}_6^-$ ($\text{X} = \text{H}$, $p\text{-OMe}$, $m\text{-OMe}$, $p\text{-Me}$, $p\text{-Cl}$, $m\text{-Cl}$, $p\text{-CO}_2\text{H}$, $p\text{-CO}_2\text{Me}$); $(\eta\text{-C}_6\text{H}_5\text{CO}_2\text{H})(\eta\text{-C}_6\text{H}_5\text{X})\text{Cr}$ ($\text{X} = \text{H}$, Cl , CF_3 , CO_2Me , CO_2H , OMe).

Introduction

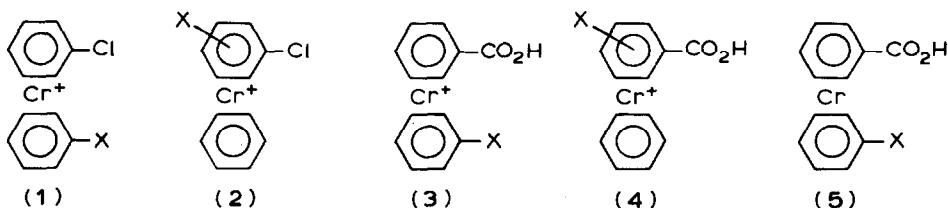
Methods for the synthesis of bis(arene)chromium complexes are important in view of both the practical utility of these compounds [1–3], and the possibility of their use as models in building a theory for the reactivity of coordinated arenes. The investigation of the effects of coordination and charge of the complexes on the

* For part XI see ref. 27.

transannular and intraligand effects of the substituents is of primary importance. Bis(arene)chromium complexes specifically enable the study of each of these effects using a single structural model. However, most of the readily available symmetric complexes of the type $(\eta\text{-RC}_6\text{H}_4\text{X})_2\text{Cr}$ differ from each other by at least two substituents, which makes interpretation of the observed effects doubtful, since upon variation of substituents R, differences in both their transannular and intraligand effects take place. Therefore, for the strict quantitative description of substituent effects on the reactivity of bis(arene)chromium complexes, one should use a series of compounds of this type which differ only by a single substituent.

Such a series of complexes may be obtained both by the general procedures which involve binding of chromium with arene ligands, and by various methods of substituent modification of the aromatic ring after coordination with chromium. The most attractive method of the first type is the low-temperature co-condensation of aromatic compounds with chromium vapours [4]; this avoids the use of Lewis acids. The need to use aluminium chloride in the Fischer-Hafner method [5-7] severely limits the possible substituents in arene.

Prior to our work, there were some examples of the synthesis of non-symmetric bis(arene)chromium complexes with polyfluorinated ligands by low-temperature co-condensation [8,9]. There were also examples of ligand modification in the bis(arene)chromium complexes mainly by processes of two types: ligand metallation by alkylolithium followed by an electrophile attack, and nucleophilic substitution of the halogen. The first procedure enables the synthesis of a number of complexes with different substituents in a polyfluorinated ligand [9,10]. Reference 8 reports nucleophilic substitution of fluorine by strong nucleophiles, such as alkylolithium, in complexes with polyfluorinated ligands. Reference 11 shows the benefits of using nucleophilic substitution of chlorine in the bis(η -chlorobenzene)chromium cation as a general route to the formation of non-symmetric complexes of the same type with electron-donating substituents. However to build up a reasonably complete theory one has to include in the analysis a series of compounds with electron-withdrawing substituents. In particular, it would be very interesting to consider chlorine containing complexes of types 1 and 2 and bis(arene)chromocarboxylic acids (3-5). Using these compounds, it is possible to study the influence of the above factors on the nucleophilic mobility of chlorine and dissociation constants in coordinated arenes. The comparison of substituent effects on these two kinds of reactivity rationalises the mechanism of nucleophilic substitution of halogen in chlorobenzene derivatives coordinated with the $(\eta\text{-PhX})\text{Cr}^+$ moiety.

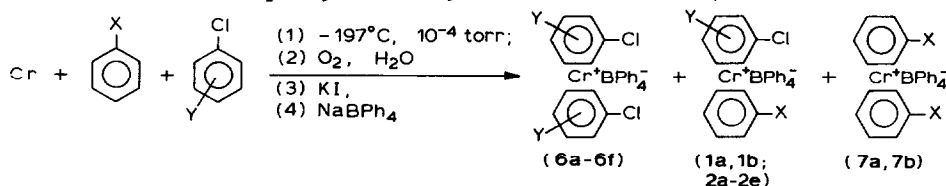


The purpose of the present work was to develop a basic approach to the synthesis of non-symmetric bis(arene)chromium complexes of types 1 to 5 based on low-temperature co-condensation of chromium vapours with arene or a mixture of arenes followed by the modification of substituents in arene ligands of the cationic complexes 1 to 4.

Results and discussion

Synthesis of the complexes 1 to 4 by low-temperature co-condensation

Non-symmetric chlorine-containing bis(arene)chromium complexes **1** and **2** were synthesized by low-temperature co-condensation of vaporized chromium with two arenes: C_6H_5Cl and C_6H_5X ($X = H, CF_3$) for complexes **1** or C_6H_6 and YC_6H_4Cl ($Y = m\text{-}Cl, p\text{-}Cl, m\text{-}OMe, m\text{-}Me, p\text{-}Me$) for complexes **2**. The resulting mixture of neutral complexes was oxidised with atmospheric oxygen in the presence of water to give cationic bis(arene)chromium complexes, which, when further converted to iodides, separated well using TLC on Al_2O_3 [12,13]. After separation the iodides were converted to tetraphenylborates by reaction with $NaBPh_4$.



complexes **1**: $X = H$ (a), CF_3 (b); $Y = H$

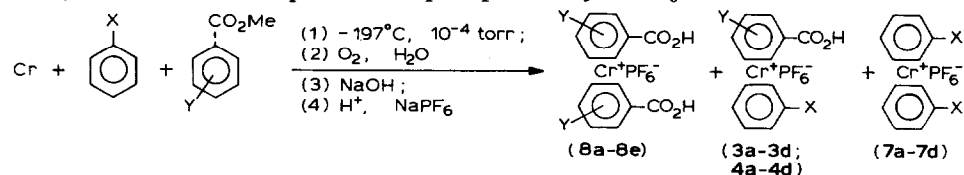
complexes **2**: $X = H$; $Y = m\text{-}Me$ (a), $p\text{-}Me$ (b), $m\text{-}OMe$ (c), $m\text{-}Cl$ (d), $p\text{-}Cl$ (e)

complexes **6**: $Y = H$ (a), $m\text{-}Me$ (b), $p\text{-}Me$ (c), $m\text{-}OMe$ (d), $m\text{-}Cl$ (e), $p\text{-}Cl$ (f)

complexes **7**: $X = H$ (a), CF_3 (b)

Yields of the complexes based on evaporated chromium were 0.1–5.8%. Such low yields in comparison with, e.g., the cation bis(η -chlorobenzene)chromium (38% [11]), bis(η -benzene)chromium (up to 60% [14]) and bis(η -benzotrifluoride)chromium (up to 26% [15]), may be partly explained by the considerable overlapping of zones of individual complexes in their TLC separation, or by the possible decomposition of complexes during separation. Compounds **6a** and **7b**, formed together with complex **1b** were isolated as a mixture, since we did not manage to separate the corresponding iodides. Complexes **6d–6f** decomposed completely during chromatographic separation on alumina, as did the individual complexes **6d** and **6f**, which were obtained by low-temperature co-condensation of chromium with the corresponding arenes.

Acids **3** and **4** were also prepared by the low-temperature co-condensation of chromium vapour with two arenes: methylbenzoate and C_6H_5X ($X = H, Me, Cl, CF_3$) for acid **3** or benzene and $YC_6H_4CO_2Me$ ($Y = m\text{-}Cl, p\text{-}Cl, p\text{-}Me, m\text{-}OMe$) for acid **4**. The ester groups in cationic complexes formed after oxidation of the condensation products were subjected to alkaline hydrolysis. The product mixtures were separated by chromatography on Al_2O_3 and, after acidification of the solutions, the individual complexes were precipitated by $NaPF_6$.



complexes **3**: $X = H$ (a), CF_3 (b), Cl (c), Me (d); $Y = H$

complexes **4**: $X = H$; $Y = m\text{-}Cl$ (a), $p\text{-}Cl$ (b), $p\text{-}Me$ (c), $m\text{-}OMe$ (d)

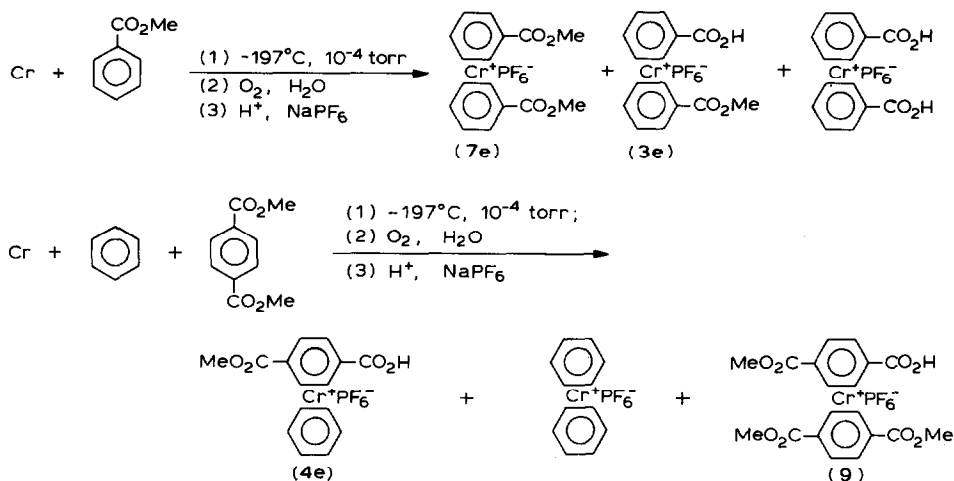
complexes **7**: $X = H$ (a), CF_3 (b), Cl (c), Me (d)

complexes **8**: $Y = H$ (a), $m\text{-}Cl$ (b), $p\text{-}Cl$ (c), $p\text{-}Me$ (d), $m\text{-}OMe$ (e)

Surprisingly, the co-condensation of chromium vapour with the benzene/methyl 2-chlorobenzoate mixture did not give the $(\eta\text{-benzene})(\eta\text{-2-chlorocarboxybenzene})\text{-chromium}$ cation, but a mixture of complexes containing no more than 14% (theoret.) of chlorine for the complex of type 4 ($Y = o\text{-Cl}$) and consisting, as indicated by the IR spectrum, mainly of complex 3a.

Using an excess of one of the arenes with respect to the other in the low-temperature co-condensation may considerably decrease the content of one of the symmetric complexes in the mixture of products, which facilitates separation of the components [16].

Due to the strong withdrawing ability of the $(\eta\text{-C}_6\text{H}_5\text{X})\text{Cr}^+$ moiety (its activating effect in nucleophilic substitution is close to that of the two nitro groups in non-coordinated arenes [11], see also ref. 17), the ester groups undergo partial hydrolysis during oxidation of neutral bis(arene)chromium complexes by atmospheric oxygen in the presence of water even at room temperature. Thus, the oxidation of the products of co-condensation of evaporated chromium with methylbenzoate, or the co-condensation with benzene and dimethylterephthalate, gave mixtures of complexes containing, in arene ligands, the methylcarboxylate and the carboxylate groups.

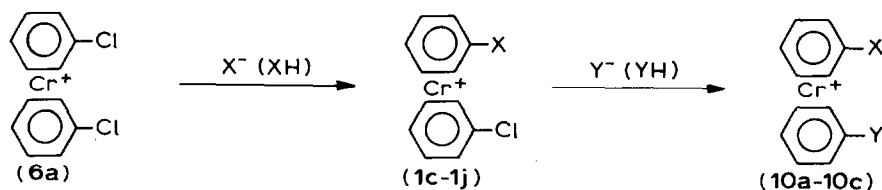


After separation of the mixtures, the components were converted to hexafluorophosphates. In the case of the co-condensation of evaporated chromium with the benzene/dimethylterephthalate mixture, only complexes with one hydrolysed ester group were isolated. It should be noted that in a previous synthesis [18] of the bis($\eta\text{-ethylbenzoate}$)chromium cation, by the same method, hydrolysis of ester groups during the course of oxidation has not been reported. The above reactions gave non-symmetric bis(arene)chromocarboxylic acids (3a–3e) and (4a–4e), symmetric bis(arene)chromodicarboxylic acids (8a–8e) and complexes 7a–7e containing no carboxylic group, in 0.7–8.5% yields.

The low-temperature co-condensation method limits slightly the possible arene substituents [19,20]. However, more non-symmetric bis(arene)chromium complexes can be made available by using the reactions which allow the modification of substituents in arene ligands of the complexes obtained by low-temperature co-condensation.

Synthesis of complexes 1 to 4 by modification of substituents in arene ligands

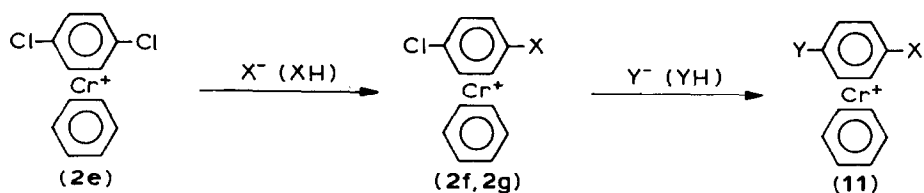
It has been found recently [11] that as a result of coordination of the chlorobenzene molecule with an $(\eta\text{-PhX})\text{Cr}^+$ moiety ($\text{X} = \text{Cl}, \text{OMe}$), the rate constant of methoxydechlorination by the action of methoxide increases up to 10^{15} times, which allows implementation of the reaction in mild conditions and isolation of the products with high yields. Moreover, a strong influence of the substituent X on the mobility of chlorine in another ligand has been found, which permits the use of the reaction for the selective substitution of one of the chlorine atoms in complex **6a** to synthesize non-symmetric bis(arene)chromium complexes. Low-temperature co-condensation followed by nucleophilic substitution reaction of the halogen with arene ligands is the essence of the present approach to synthesising a series of symmetric and non-symmetric bis(arene)chromium complexes with different substituents. For complex **2e**, we have also found the possibility for successive substitution of chlorine atoms with sodium methoxide. In this connection it is noteworthy that bis(η -fluorobenzene)chromium(0) undergoes nucleophilic substitution with methoxide under more rigid conditions ($40\text{--}45^\circ\text{C}$, 14 h), with loss of both fluorines. The reaction gave a very low yield of bis(methoxybenzene)chromium(0) [8]. We used selective substitution of one of the chlorine atoms in complexes **6a** and **2e** with aliphatic alkoxides and amines to synthesize non-symmetric bis(arene)chromium complexes of types 1 and 2.



complexes 1: $\text{X} = \text{MeO}(\text{c}), \text{EtO}(\text{d}), \text{i-PrO}(\text{e}), \text{n-BuO}(\text{f})$;

$\text{XH} = \text{C}_6\text{H}_{11}\text{NH}(\text{g}), \text{C}_6\text{H}_9\text{NH}(\text{h}), \text{Me}_2\text{NH}(\text{i}), \text{C}_6\text{H}_{11}\text{NH}_2(\text{j})$

complexes 10: $\text{X} = \text{n-BuO}(\text{a}), \text{i-PrO}(\text{b}), \text{Me}_2\text{N}(\text{c})$; $\text{Y} = \text{MeO}$



complex 2: $\text{X} = \text{MeO}(\text{f})$; $\text{XH} = \text{HNMe}_2(\text{g})$

complex 11: $\text{X} = \text{NMe}_2$, $\text{Y} = \text{MeO}$

The reactions with amines were carried out in acetone, and those with alkoxides, in the appropriate alcohols. Because of a sharp decrease in the solubility of **6a** in higher alcohols, the latter were used with small admixtures of acetonitrile. Addition of acetonitrile was also found to promote the substitution of chlorine.

Substitution of one chlorine atom in **6a** and **2e** in the reactions with the above nucleophiles considerably retarded substitution of the other halogen. This may be used for the stepwise substitution of both halogen atoms to obtain complexes with

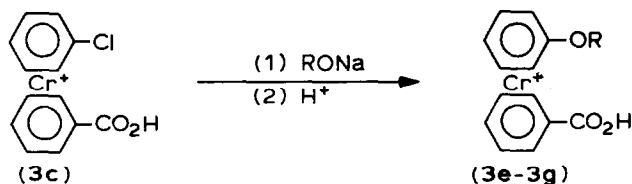
TABLE 1
REACTION CONDITIONS OF LOW TEMPERATURE CO-CONDENSATION OF CHROMIUM WITH BENZENE AND $\text{XC}_6\text{H}_4\text{Y}$

Entry	X	Y	Arene (g)		Evaporated chromium (g)	Vaporization time (min)	Yield (%) ^{a,b}		
			C_6H_6	$\text{XC}_6\text{H}_4\text{Y}$			$(\eta\text{-C}_6\text{H}_5)_2\text{Cr}^+\text{A}^-$	$(\eta\text{-C}_6\text{H}_5)(\eta\text{-ZC}_6\text{H}_4\text{Y})\text{Cr}^+\text{A}^-$	$(\eta\text{-ZC}_6\text{H}_4\text{Y})_2\text{Cr}^+\text{A}^-$
1	Cl	<i>m</i> -OMe	—	80	0.83	50	—	—	8.8
2	Cl	<i>p</i> -Cl	—	72	0.74	60	—	—	6.3
3	Cl	<i>p</i> -Cl	70	135	0.75	55	5.8	4.6	c
4	Cl	<i>m</i> -Cl	49	91	1.1	55	/	1.9	c
5	Cl	<i>p</i> -Me	49	80	1.1	50	/	1.9	1.0
6	Cl	<i>m</i> -Me	49	80	1.1	70	/	3.7	2.4
7	Cl	<i>m</i> -OMe	70	127	0.72	45	4.6	3.3	c
8	CO_2Me	<i>p</i> -Cl	50	112	0.93	60	3.1	4.3	1.2
9	CO_2Me	<i>m</i> -Cl	47	103	0.89	40	1.5	2.2	1.1
10	CO_2Me	<i>o</i> -Cl	52	117	0.79	36	1.2	d	d
11	CO_2Me	<i>p</i> -Me	44	87	0.61	35	2.8	4.2	2.2
12	CO_2Me	<i>m</i> -OMe	38	81	0.71	43	2.0	2.7	1.9
13	CO_2Me	<i>p</i> - CO_2Me	55	139	0.90	51	—	2.1	1.3 ^e

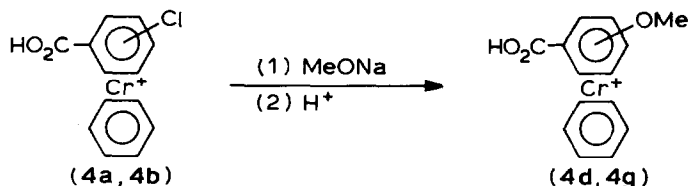
^a Entry 1-7 Z = Cl; entry 8-13 Z = CO_2H . ^b Entry 1 and 4-7 $\text{A}^- = \text{Ph}_4^-$; entry 2, 3 and 8-13 $\text{A}^- = \text{PF}_6^-$. ^c The complex decomposed during isolation. ^d The products contain ~14% of chlorine (theor.) for $(\eta\text{-C}_6\text{H}_5)(\eta\text{-2-ClC}_6\text{H}_4\text{CO}_2\text{H})\text{Cr}^+\text{PF}_6^-$ and $(\eta\text{-2-ClC}_6\text{H}_4\text{CO}_2\text{H})_2\text{Cr}^+\text{PF}_6^-$. ^e Complex $[\eta\text{-4-(CO}_2\text{Me)}_2\text{C}_6\text{H}_4]\text{Cr}^+\text{PF}_6^-$. ^f The complex was not isolated.

different substituents in the ligands. Thus substitution of chlorine atoms in complexes **1e**, **1f**, **1i** and **2i** by the methoxy group gave complexes **10a–10c** and **11**. The scheme of transformations of complexes **6a** and **2e** was realized for a wide range of various modifications of arene ligands. This allows the consideration of nucleophilic substitution of halogen atoms in bis(arene)chromium cations to be a rather general method for the preparation of compounds of this type with various substituents in arene ligands.

Ligand modification in the acids **3c** and **4a**, **4b** by nucleophilic substitution of chlorine has been shown to occur in their reactions with alkoxides in alcohol/acetonitrile (9/1) mixtures at 23°C.



$\text{R} = \text{Me}(\text{e}), i\text{-Pr}(\text{f}), n\text{-Bu}(\text{g})$



As shown by the amount of chloride ion released, all the reactions went to completion. The substitution products appeared, however, to be unstable and partially decomposed upon isolation. The use of an inert atmosphere gave yields of 49–93%.

This method for the preparation of bis(arene)chromium complexes offers some advantages over the method of preparing the same complexes by low-temperature co-condensation alone. Not only does it lead to higher yields of symmetric complexes containing alkoxy or dialkylamino groups in arene ligands than the low-temperature co-condensation [17,21,22], it also has the important advantage that it allows complexes to be obtained which contain substituents with an active hydrogen, e.g. **1j**, the synthesis of which is questionable by other methods.

(Continued on p. 198)

TABLE 2

REACTION CONDITIONS OF NUCLEOPHILIC SUBSTITUTION OF CHLORINE IN $(\eta\text{-C}_6\text{H}_6)(\eta\text{-XC}_6\text{H}_4\text{Cl})\text{Cr}^+$ AT 23°C

X	Nucleophile	Concentrations (mol/l)		Reaction time (h)	Isolated complex yield (%)
		Complex	Nucleophile		
<i>p</i> -Cl	MeONa	2.9×10^{-3}	4.0×10^{-3}	1.0	2f (77)
<i>p</i> -Cl	Me_2NH	1.6×10^{-2}	2.3	0.5	2g (67)
<i>p</i> -NMe ₂	MeONa	5.0×10^{-3}	1.2×10^{-1}	24.0	11 (84)
<i>p</i> -CO ₂ H	MeONa	3.6×10^{-3}	1.1×10^{-2}	3.5	4f (62)
<i>m</i> -CO ₂ H	MeONa	3.6×10^{-3}	1.1×10^{-2}	3.0	4d (56)

TABLE 3
ANALYTICAL AND SPECTRAL DATA FOR $(\eta\text{-C}_6\text{H}_6\text{X})(\eta\text{-XC}_6\text{H}_4\text{Y})\text{Cr}^+\text{A}^-$

No.	X	Y	A	Analysis (Found (calcd.) (%)) ^a				Spectral data						
				C	H	F	Cl	ESR <i>a</i> _H (G)	UV ^b λ _{max} (nm) (log ε)	IR ($\bar{\nu}$, cm ⁻¹) ^{c,d}				
										Cr-Ar	C-C arene	C-H	C=O	C-O
2e	Cl	<i>p</i> -Cl	PF ₆	34.1 (34.1)	2.2 (2.4)	27.3 (27.0)	16.7 (16.8)	3.5	286(3.75) 349(3.79)	430 475	1440	3105	-	-
2d	Cl	<i>m</i> -Cl	BPh ₄	72.0 (72.5)	5.0 (5.1)	-	12.5 (11.9)	3.7	350(3.81)	430 475	1470	-	-	-
2b	Cl	<i>p</i> -Me	BPh ₄	77.7 (77.2)	6.0 (5.8)	-	6.2 (6.2)	3.4	345(3.82)	430 475	1450	-	-	-
2a	Cl	<i>m</i> -Me	BPh ₄	77.8 (77.2)	5.9 (5.8)	-	5.7 (6.2)	3.5	345(3.83)	430 470	1440	-	-	-
2c	Cl	<i>m</i> -OMe	BPh ₄	75.2 (75.1)	5.5 (5.6)	-	5.9 (6.0)	3.7	348(3.79)	425 465	1460 1530	2855	-	1260
2f	Cl	<i>p</i> -OMe	BPh ₄	75.2 (75.1)	5.7 (5.6)	-	5.8 (6.0)	3.6	349(3.82)	430 465	1435 1460 1485	2840	-	1255
2g	Cl	<i>p</i> -NMe ₂	BPh ₄	75.4 (75.4)	6.1 (6.0)	-	5.9 (5.9)	3.8	361(3.76)	430 450 480	1525 1435 1465 1490 1550	-	-	-
2i	Cl	<i>p</i> -CO ₂ Me	PF ₆	37.9 (37.7)	3.0 (2.9)	25.7 (25.6)	7.8 (8.0)	3.4	279(3.68) 312(3.60) 350(3.73)	425 460 545	1440 1485	2970 3100	1725	1120 1290

2h	Cl	<i>m</i> -CO ₂ Me	PF ₆	37.7 (37.7)	3.0 (2.9)	25.6 (25.6)	7.9 (8.0)	3.5	281(3.75) 307(3.68) 352(3.75)	435 475	1440 1465	2965 3105	1725	1295
4b	Cl	<i>p</i> -CO ₂ H	PF ₆	36.1 (36.2)	2.5 (2.6)	26.6 (26.4)	8.1 (8.2)	3.5	279(3.69) 304(3.52) 350(3.71)	425 465 540	1445 1490 1420	3110	1720	1300
4a	Cl	<i>m</i> -CO ₂ H	PF ₆	36.1 (36.2)	2.5 (2.6)	26.6 (26.4)	8.3 (8.2)	3.4	281(3.78) 349(3.79)	435 475	1445	3100	1715	1300
4c	CO ₂ H	<i>p</i> -Me	PF ₆	40.8 (40.9)	3.4 (3.4)	27.9 (27.7)	—	3.5	281(3.72) 350(3.74)	425 460	1420 1460	3105	1715	1270 1300
4f	CO ₂ H	<i>p</i> -OMe	PF ₆	39.4 (39.4)	3.2 (3.3)	26.6 (26.7)	—	3.6	278(3.69) 349(3.71)	425	1420 1435	2850 3110	1715	1260 1300
4d	CO ₂ H	<i>m</i> -OMe	PF ₆	39.4 (39.4)	3.2 (3.3)	26.8 (26.7)	—	3.5	281(3.68) 354(3.70)	430 465	1430 1485	3105	1700	1250 1270
4e	CO ₂ H	<i>p</i> -CO ₂ Me	PF ₆	39.5 (39.6)	3.2 (3.1)	25.2 (25.0)	—	3.3	277(3.57) 318(3.53) 348(3.58)	410 495 520	1430 1450	3095	1700 1725	1270
4g	CO ₂ H	<i>p</i> -CO ₂ H	PF ₆	38.0 (38.1)	2.7 (2.7)	25.9 (25.8)	—	3.3	277(3.40) 318(3.35) 348(3.39)	430 525	1445 1465	3100	1715	1295
11	OMe	<i>p</i> -NMe ₂	BPh ₄	77.8 (78.0)	6.8 (6.7)	—	—	3.7	364(3.68)	430 465	1455 1535	—	—	1150 1255

^a Nitrogen analysis: found (calcd.): **2h** 2.4(2.3); **11** 2.3(2.3). ^b Spectra of tetraphenylborates run in MeCN; acids run in H₂O; others in EtOH. ^c Absorption bands of counterions are not given. BPh₄[−] counterion absorption makes it impossible to determine the position of the bands corresponding to C–H vibrations. ^d For complex **2g** $\bar{\nu}$ (C–N) 1225 cm^{−1}

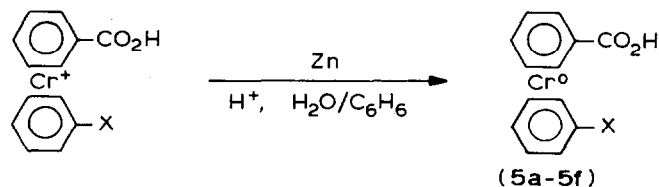
Other types of reaction that allow modification of the substituents in arene ligands of bis(arene)chromium cations, are the reactions of the carboxylic and alkylcarboxylate groups. When we began our work it was known that the carboxylic group in neutral bis(arene)chromium complexes is easily esterified by dimethyl sulphate and diazomethane, and that the alkylcarboxylate group readily undergoes alkaline hydrolysis and transesterification [23,24]. We have now shown that such reactions can be used for the modification of substituents in cationic bis(arene)chromium complexes. Thus esterification of the acids **3c**, **4a**, **4b** by diazomethane gave the respective methyl ethers **1k**, **2h**, **2i** in 79–90% yields.

Alkaline hydrolysis of the ester groups in complexes **4e** and **9** with subsequent acidification of the reaction mixtures gave (η -benzene)(η -*p*-dicarboxybenzene)chromium (**4g**) and bis(η -*p*-dicarboxybenzene)chromium (**12**) hexafluorophosphates, in 83 and 78% yields, respectively.

The cationic bis(arene)chromium complexes, isolated as hexafluorophosphates or tetraphenylborates, are yellow or orange-yellow crystalline substances. Tetraphenylborates are soluble in polar, aprotic solvents, and the hexafluorophosphates are also soluble in methanol, ethanol and water. The coordinated carboxylic acids are stable in acid media up to pH = 1, whereas the complexes containing no carboxyl decompose readily upon acidification, their solutions changing colour from yellow to green, and a dark precipitate formed. Solutions of complexes containing the amino group, particularly those of complexes **10c** and **11**, are unstable in air; several minutes after their solution in acetonitrile, a brown precipitate is formed and the solution changes colour from yellow to emerald green. The solutions of other complexes under similar conditions do not undergo any visible changes after an hour. The cationic complexes obtained have no definite temperature at which decomposition occurs and it depends on the rate of sample heating and/or the particle size of the complexes. Heating leads to decomposition of the complexes within the temperature range 150–200°C. Long storage in air at room temperature also results in decomposition of the complexes, as indicated by a change in colour from yellow-orange to green (for hexafluorophosphates) or to grey (for tetraphenylborates). To avoid decomposition of the complexes, they were stored between –80 for –100°C.

Synthesis of bis(arene)chromo(0) carboxylic acids (5)

Reduction of the appropriate cationic complexes by zinc in acid medium at room temperature [25] gave the bis(arene)chromo(0) carboxylic acids.



X = H(**a**), Cl(**b**), CF₃(**c**), CO₂Me(**d**), CO₂H(**e**), OMe(**f**)

Yields of the complexes were rather high, 76 to 91%, with the exception of the acid **5d** (28%).

The neutral bis(arene)chromo(0) carboxylic acids were crystalline compounds, orange to violet-red in colour, soluble in benzene, alcohols and bipolar aprotic

TABLE 4. ANALYTICAL AND SPECTRAL DATA FOR $(\eta\text{-XC}_6\text{H}_4\text{Y})(\eta\text{-XC}_6\text{H}_4\text{Z})\text{Cr}^+\text{A}^-$ ^a

No.	X	Y	Z	Analysis (Found (calcd.)) (%)				Spectral data						
				C	H	F	Cl	ESR $a_{\text{H}}(\text{G})$	UV ^b $\lambda_{\text{max.}}(\text{nm})$ (lg ϵ)	IR ($\bar{\nu}$, cm ⁻¹) ^c				
										Cr-Ar	C-C arene	C-H	C=O	C-O
6f	Cl	p-Cl	p-Cl	29.5 (29.4)	1.7 (1.6)	23.3 (23.2)	28.8 (28.9)	4.0	290(3.62) 358(3.51)	420 475	1445	3100	-	-
6c	Cl	p-Me	p-Me	72.5 (73.1)	6.0 (5.5)	-	11.4 (11.4)	3.8	353(3.81)	430 465	1440	-	-	-
6b	Cl	m-Me	m-Me	73.3 (73.1)	5.7 (5.5)	-	10.9 (11.4)	3.8	354(3.79)	415 470	1450	-	-	-
6d	Cl	m-OMe	m-OMe	69.4 (69.5)	5.4 (5.2)	-	10.6 (10.8)	4.0	357(3.72)	425 465	1460 1525	-	-	1260
8b	CO ₂ H	m-Cl	m-Cl	32.8 (33.0)	1.9 (2.0)	22.5 (22.4)	14.0 (13.9)	3.5	287(3.72) 357(3.70)	435 475	1420 1445	3105	1715	1300
8c	CO ₂ H	p-Cl	p-Cl	33.0 (33.0)	2.1 (2.0)	22.2 (22.4)	13.8 (13.9)	3.5	285(3.68) 358(3.66)	430 475	1420 1445	3100	1715	1300
8d	CO ₂ H	p-Me	p-Me	41.1 (41.0)	3.5 (3.4)	24.4 (24.3)	-	3.5	286(3.78) 358(3.78)	425 440	1415 1475	3105	1710	1295
8e	CO ₂ H	m-OMe	m-OMe	38.5 (38.3)	3.3 (3.2)	22.6 (22.7)	-	3.6	287(3.71) 358(3.72)	425 465	1420 1520	3105	1705	1260 1295
12	CO ₂ H	p-CO ₂ H	p-CO ₂ H	36.2 (36.3)	3.3 (3.2)	19.8 (20.0)	-	3.2	278(3.77) 321(3.73)	430 520	1420 1445	3105	1720	1145 1305
9	CO ₂ Me	p-CO ₂ H	p-CO ₂ Me	40.0 (39.9)	2.2 (2.3)	21.7 (21.5)	-	3.4	275(3.62) 324(3.72)	430 520	1420 1445	3105	1720	1145 1305
									347(3.65) 412(3.23)		1470			

^a A⁻ = BPh₄⁻ for complexes 6b-6d, in other instances A⁻ = PF₆⁻. ^{b,c} See notes b, c to Table 3.

solvents. The neutral acids were readily oxidized in air and were therefore handled, only in an inert atmosphere. On heating, these compounds behave in an unusual way. When a sample of the acid was placed in a sealed capillary or between two glass plates under argon, on a surface heated to 130–150°C, the crystals quickly melted (except the acid **5e**), the melt solidified and at 200–250°C changed colour from red to green, obviously due to decomposition. Upon slow heating of the sample from room temperature to 60–100°C, slight melting of the crystal edges occurred, further heating (to 250°C) caused a slow change in colour.

Thus the use of low-temperature co-condensation in combination with nucleophilic substitution of chlorine and reactions modifying the carboxyl and alkylcarboxylate groups in arene ligands of bis(arene)chromium cationic complexes, gave a series of complexes **1–5** with a varied substituent X in the arene ligands. These models were necessary for detailed investigation of the nucleophilic substitution of halogen in bis(arene)chromium complexes and the pK_a values of similarly coordinated benzoic acids to rationalise the mechanism of the reactions of coordinated arenes with nucleophiles. Research on this topic is continuing.

Experimental

For general remarks, see ref. 16; the same reference reports procedures for the preparation of complexes **1** and **3**. Synthesis of complexes **2** and **4** were carried out by similar procedures. The experimental results for the synthesis of complexes **2** and **4** are summarised in Tables 1 and 2, and characteristics of the products are summarised in Tables 3 and 4. The synthesis of complex **5** is described in [26].

*(η -Benzene)(η -*p*-dicarboxybenzene)chromium cation*

Complex **4e** (100.3 mg, 22 mmol) was added to 15 ml of 0.1 *N* (150 mmol) aqueous NaOH solution and after 15 min the solution was neutralised with 0.1 *N* HCl. Then 0.5 g of NaPF₆ was added, and to the resulting solution, 5% aqueous HCl was added dropwise until pH 1–2. The precipitate was filtered off and dissolved in 50 ml MeCN. For complete isolation of the product the mother solution was extracted with CH₂Cl₂. The combined solutions were evaporated and the product was precipitated by adding diethyl ether. The precipitate was filtered off and dried under argon to give 80.5 mg (18.5 mmol) of complex **4g** (83% yield).

Complex **12** was obtained by a similar procedure. Yield 78%.

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