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BIS(ARENE)METAL COMPOUNDS

I. NUCLEOPHILIC SUBSTITUTION OF BIS(η^6-CHLOROBENZOTRIFLUORIDE)CHROMIUM(0) WITH THIOPHENOXIDE

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Summary

The *ortho, meta* and *para* complexes of bis(η^6-chlorobenzotrifluoride)-chromium(0) were made by metal-vapor synthesis. Nucleophilic substitutions by thiophenoxide of these complexes are compared to nucleophilic substitutions by thiophenoxide on the uncoordinated arenes. It was found that substitution at the chloro position is more facile on the complexes than on the free arenes. Substitution of the chloro on the *meta*-isomer sandwich was more facile than substitution of the chloro on the *ortho*-isomer sandwich, contrary to the observed reactivity pattern in the free arenes.

Introduction

The metal-vapor synthesis technique allows synthesis of bis(arene)chromium(0) compounds with a variety of substituents on the ring [1]. Such compounds have been the subject of numerous investigations since the application of the metal-vapor synthesis technique has made a large number of compounds with substituents as diverse as chloro, methyl, methoxy, dimethylamino and methylbenzoate readily available [1–6]. However, some arenes of interest, such as aniline [2], pyridine [2], acetophenone [2], and benzonitrile [2,7], are either isolated in low yields [7] or not obtainable [2] as the bis(arene)chromium(0) sandwich. An alternative route to the synthesis of these compounds would be attractive. One such route would be nucleophilic substitution of a substituent that can be made by the metal-vapor technique by an appropriate nucleophile [8]. A better understanding of nucleophilic substitution on the rings of these complexes would be helpful in allowing the design

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of the rational synthesis of bis(arene)chromium(0) compounds with desired substituents.

The extent of aromaticity in arenes is dependent upon the definition of aromaticity used. One measure of increased aromaticity could be increased susceptibility to electrophilic substitution and decreased susceptibility to nucleophilic attack. Compared to the free arene, bis(arene)chromium(0) compounds are reported to have shown reduced reactivity to electrophiles [9,10]. This decreased reactivity would seem to indicate that the complexed ring is "less aromatic" than the free arene [2]. For nucleophiles the situation is less straightforward, since methoxide substitution at a fluorine atom in hexafluorobenzene does not occur as readily in the chromium complex as in the free arene, whereas carbanion substitution at a fluorine atom in hexafluorobenzene appears to occur more readily on the arene in the chromium complex than on the free arene [11]. These ambiguous results are not consistent with the expectation that nucleophilic substitution should become easier with decreased aromaticity. This behavior is in contrast to arene-chromiumtricarbonyls, which show increased reactivities to all nucleophiles tested to date [12]. A greater number of examples of nucleophilic reactions of bis(arene)chromium(0) compounds should help resolve this dilemma.

For uncomplexed arenes there is enhanced nucleophilic substitution if the site of substitution is either *ortho* or *para* to a nucleophilic activating group, such as the trifluoromethyl group [13]. Is there a modification of this effect when the arene is in a metal sandwich complex? Reaction of n-butyllithium with hexafluorobenzene results in the same product (1,2,4,5-tetrakis(n-butyl)-3,6-difluorobenzene) for both chromium-complexed and free hexafluorobenzenes [11], leading one to suspect substitution preference patterns will prove to be the same for both the complexed and free arenes. Presently there is not enough evidence to support this assertion.

This work was undertaken so that nucleophilic substitution in bis(arene)chromium(0) complexes could be better understood. An increased understanding of nucleophilic substitution may pave the road to the synthesis of bis(arene)chromium(0) complexes that cannot be obtained by the techniques now available [8]. Furthermore, knowledge of the changes in reactivity of an arene ring, caused by the complexation to chromium in a sandwich compound, may lead to further evidence regarding aromaticity in sandwich complexes.

Experimental

Metal atom reactor. A metal vapor synthesis apparatus similar to that of Klabunde [14,15] was built. The stainless steel reaction head has a 4-inch diameter valve to the oil diffusion pump, allowing an easily-attainable vacuum of 0.1 μtorr. Typically the pressures in the 4-l reaction flask during a reaction were kept between 10 and 100 μtorr.

The metal vaporization was done with a 75 A step-down transformer applied across tungsten coils (R.D. Mathis Company, B12 13-.04W) attached via 1/4 inch water-cooled copper electrodes. Ligand deposition was accomplished through a vacuum manifold inlet assembly.

Metal vaporization reactions

Typical preparations of the bis(arene)chromium complexes are as described elsewhere [2], except no attempt was made to maintain an inert atmosphere. Yields are minimum estimates, based on total metal vaporized; actual yields may be as much as 30% higher [2]. Yields were occasionally lower than those published [4], probably due to an exothermic reaction of colloidal chromium with oxygen upon exposure to air [2], since a brown or grey smoke was often observed prior to sublimation of product [16]. This was particularly true for the *ortho* isomer. Colors of these complexes depend to some extent on the thickness of the crystals; thinner crystals appearing yellow-green for each of the isomers; thicker crystals taking on a red-brown hue. All the complexes had a fragrant pine-needle odor, and they all sublimed at 60–80°C and 1.0 mtorr.

Bis(η^6*-o-chlorobenzotrifluoride)chromium(0).* This complex is air-stable, m.p. 81.5–84.0°C, ref. 4: 81.0–82.5°C. Yield was 2% (0.22 g). Mass spectrum for EI (chloro isotope pattern excluded), 70 eV; 107 (C_6H_4CF, 36.1), 126 ($C_6H_4CF_2$, 48.2), 161 ($C_6H_4ClCF_2$, 100.0), 232 ($CrC_6H_4ClCF_3$, 47.8), 377 ($M-Cl$, 18.0), 412 (M, 57.2); for CI, 70 eV; 344 ($M-2Cl$, 22.1), 378 ($M-Cl+H$, 71.5), 412 (M, 100.0) was found. The IR is consistent with the reported data [4].

Bis(η^6*-m-chlorobenzotrifluoride)chromium(0).* This complex is air-stable, m.p. 73.0–77.0°C. Yield was 8% (0.44 g). Mass spectrum for EI (chloro isotope pattern excluded), 70 eV; 52 (Cr, 76.0), 126 ($C_6H_4CF_2$, 32.6), 161 ($C_6H_4ClCF_2$, 100.0) 232 ($CrC_6H_4ClCF_3$, 29.1), 377 (M-Cl, 11.3), 412 (M, 25.0); for CI, 70 eV; 378 ($M-Cl+H$, 19.5), 412 (M, 100.0) was found. IR in KBr pellet: 3065m, 1520m, 1472w, 1455w, 1425w, 1398w, 1369m, 1313m, 1300s, 1261m, 1173s, 1150s, 1120s, 1104s, 1070s, 1042s, 980m, 930w, 881w, 877w, 832m, 826m, 802m, 710m, 699m, 678m, 652m, 575w, 492s, 470s, 450s, 407m, 377w, 318m.

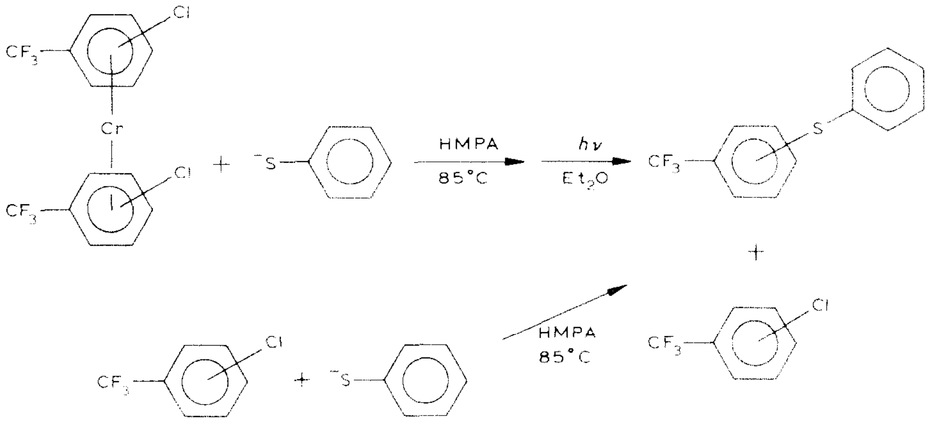
Bis(η^6*-p-chlorobenzotrifluoride)chromium(0).* This complex is air-stable, m.p. 81.0–82.0°C, ref. 2: 80.5–82.5°C. Yield was 35% (0.81 g). Mass spectrum for EI (chloro isotope pattern excluded), 70 eV; 52 (Cr, 24.1), 126 ($C_6H_4CF_2$, 23.2), 161 ($C_6H_4ClCF_2$, 100.0), 232 ($CrC_6H_4ClCF_3$, 8.7), 412 (M, 9.2); for CI, 70 EV; 378 ($M-Cl+H$, 4.8), 412 (M, 100.0) was found. The IR is consistent with the reported data [17].

Reactions

The reactions of the three isomers of chlorobenzotrifluoride with thiophenoxide were carried out under conditions similar to those reported by Cogolli et al. [18] In each case the hexamethylphosphoramide (HMPA) solution containing 0.2 M arene and 0.6 M sodium thiophenoxide was heated for 2 h, under nitrogen, at 85°C. The HMPA solution was then cooled, diluted with water, and the product extracted with ether. Flash vaporization of the ether solution, after drying over sodium sulfate, yielded a solution which was then analyzed by GLC and GC/MS.

The reactions of the three isomers of the bis(arene)chromium(0) complexes with thiophenoxide were conducted similarly, except that the initial concentration of complex was 0.1 M. The HMPA solution was cooled, diluted with water and the product extracted with ether. Vaporization of ether resulted in a dark brown solid or oil. No evidence of complex decomposition at this point was observed, but decomposition of this solid occurred with time. The chromium complexes were deliberately decomposed (usually by photolysis) to yield the thiophenoxybenzotrifluorides and the chlorobenzotrifluorides, which were then analyzed by GLC and GC/MS.

Scheme 1 shows the general procedures described above.



SCHEME 1

Bis(η^6-p-thiophenoxybenzotrifluoride)chromium(0). Reaction of the *p*-chlorobenzotrifluoridechromium complex (0.62 g) with thiophenoxide (1.19 g) in HMPA (15 ml) was conducted as described above. The ether extract was placed under a mtorr vacuum for 22 h. The complex is a weakly air-sensitive brown oil. Yield was 78% (0.66 g). Mass spectrum for EI, 70 eV: 235 ($CF_3C_6H_4SC_6H_5$, 41.6), 306 ($CrCF_3C_6H_4SC_6H_5$, 16.3), 560 (*M*, 100.0); for CI, 70 eV; 560 (*M*, 100.0) was found. IR neat between NaCl plates: 3080m, 1940w, 1790w, 1725w, 1660w, 1578s, 1512m, 1473s, 1435s, 1339m, 1310s, 1165s, 1120s, 1070s, 1045s, 1020s, 991s, 890w, 825m, 772m, 735s, 683s, 602w, 578m.

Instrumental. The GLC were done using OV-101 columns with a programmed temperature ramp from 80–180°C. The GC/MS and MS were recorded with a Finnigan 4000 and a Finnigan 9610 INCOS data system.

The IR spectra were taken on a Perkin–Elmer 683 spectrometer.

Results

There was no scrambling of substituent positions during the reactions of the free arenes nor during the reactions of the complexed arenes. There was no evidence of the formation of oxidized sandwich compound during the course of the reaction (2 h), although the products would show signs of decomposition after a day.

Isolation of the chromium-complexed product was attempted for some reactions. The brown material isolated from the reaction of bis(η^6-*m*-chlorobenzotrifluoride)chromium(0) with three-fold excess sodium thiophenoxide proved to contain (by MS) bis(η^6-*m*-chlorobenzotrifluoride)chromium(0) with some (η^6-*m*-chlorobenzotrifluoride)(η^6-*m*-thiophenoxybenzotrifluoride)chromium(0). No bis(η^6-*m*-thiophenoxybenzotrifluoride)chromium(0) was detected, but this does not mean that none was made, since this product would be more likely to decompose readily than the starting material, and some decomposition may have occurred before the MS was taken.

The bis(η^6-*p*-thiophenoxybenzotrifluoride)chromium(0) product was also investigated. It was found to contain the impurities (by MS) bis(η^6-*p*-chlorobenzotrifluoride)chromium(0), (η^6-*p*-chlorobenzotrifluoride)(η^6-*p*-thiophenoxybenzotrifluoride)chromium(0) and diphenyldisulfide, an impurity in the sodium thiophenoxide that was used. The IR results indicated that the impurities were present in acceptable

TABLE 1

REACTION YIELDS [a]

Substituent ring position	Free arene reaction yields		Complexed arene reaction yields	
	reactant [b]	product [c]	reactant [b]	product [c]
ortho	87.0	10.8	69.8	30.2
meta	87.9	2.6	48.8	41.8
para	40.4	58.6	3.9 [d]	86.5

[a] Yields are for total free arene recovered, and are based on GC peak areas. [b] $CF_3C_6H_4Cl$. [c] $CF_3C_6H_4SC_6H_5$. [d] For some reactions no reactant detected.

quantity (< 5%). There was no evidence of benzotrifluoride or free *p*-phenoxybenzotrifluoride in the oil.

It was decided that the most consistent results could be obtained by deliberate decomposition of the chromium-complexed product, as shown in Scheme 1.

Yields in Table 1 do not add up to 100% because of contamination of starting material with other isomers, and due to benzotrifluoride in the reacton mixture of the chromium-complexed *para*-substituted (8.7%) and the chromium-complexed *meta*-substituted reaction (3.9%).

The results of the reactions with thiophenoxide are shown in Table 1. It is clear from Table 1 that, compared to the free arene, there is an increase in susceptibility to nucleophilic attack for the complexed arene of about 3.6 for the *ortho*-, about 16 for the *meta*-, and about 1.6 for the *para*-substituted chlorobenzotrifluoride. In addition, Table 1 shows that the pattern of susceptibility to nucleophilic attack has changed upon complexation.

Discussion

Clearly there is a significant enhancement of susceptibility to nucleophilic attack at the chloro position in all of the isomers, but the largest enhancement upon coordination occurs for the *meta* isomer. This enhancement of substitution in the system of a thiophenoxide nucleophile and a chloride leaving group contrasts with the observation of decreased susceptibility to nucleophilic substitution in the system of a methoxide nucleophile and a fluoride leaving group [11]. In addition, it has been observed that bis(η^6-*p*-chlorobenzotrifluoride)chromium(0) reacts readily with ethoxide to substitute the chloro group with an ethoxy group [19]. A tentative conclusion could be that susceptibility to nucleophilic substitution is increased in bis(arene)chromium(0) complexes when compared to the free arene if the leaving group is a chloride ion, but decreased when the leaving group is a fluoride ion.

In Table 1 it can be observed that for the uncomplexed arene one has the expected pattern of enhanced attack in the *ortho* and *para* positions, whereas for the π-complexed arene the pattern of enhanced attack is *ortho* < *metal* < *para*. This pattern may be due to the greater steric hindrance at the *ortho* position in the chromium complex as compared to the free arene. Alternatively, electronic effects may be responsible.

It is interesting to note that on the related bis(η^6-chlorobenzene)chromium(I) cation nucleophilic substitutions also proceed more readily than for chlorobenzene [20]. It would, however, be expected that the cation would tend to withdraw electron density from the ring, making the likelihood of increased susceptibility to nucleophilic attack more probable than for the neutral chromium complex.

The reactivity of the chloride substituent on an arene toward the nucleophile, thiophenoxide, is increased when the chloro-arene is complexed with chromium in a sandwich compound. This enhancement of susceptibility to nucleophilic substitution implies a decrease aromaticity of the arene ring upon complexation. There also appears to be a change in the positional susceptibility to nucleophilic substitution, the *meta* complex increasing in susceptibility on complexation much more than either the *para* or *ortho* isomers. Nucleophilic substitution of bis(arene)chromium(0) complexes appears to be a reasonable route for the synthesis of new bis(arene)chromium(0) compounds that cannot be made by other methods.

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