COMPLEXES OF METALS WITH AROMATIC SYSTEMS

LXXXIV*. ANTHRACENECHROMIUM TRICARBONYL**

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INTRODUCTION

Since the discovery that aromatic ligands are capable of forming π-bonded me carbonyl derivatives[3], there has been interest in the preparation and the determination of the structures of such complexes of condensed ring aromatic compounds. Among the complexes studied have been the Group VI metal carbonyls of naphthalene, indene, phenanthrene, acenaphthylene, pyrene and chrysene[4,5].

One of the most difficult of complexes of this type to prepare and characterize is anthracenechromium tricarbonyl. This compound was first prepared in these laboratories[5]. However, because it tends to decompose rather readily, it was not possible to isolate it in a pure state, and the amount of compound available was not sufficient for its characterization. The identification was made spectroscopically. The preparation of this complex is also claimed in a patent[6]. However, no properties are given (nor have they been published subsequently), and attempts to reproduce the synthesis under the specified conditions were unsuccessful. The preparation and characterization of this compound are reported here.

EXPERIMENTAL

Materials

Chromium hexacarbonyl was prepared as previously described[7]. Anthracene was a resublimed commercial product. All solvents were dried over sodium, saturated with nitrogen, distilled, and stored under nitrogen and over sodium.

Procedure

The apparatus used was designed to enable the $Cr(CO)_6$ which sublimes during the course of the reaction to be returned continuously to the reaction flask[8]. In the apparatus were placed 2.5 g (11.4 mmole) $Cr(CO)_6$ and 2.5 g (14.0 mmole) $C_{14}H_{10}$; the air was removed by successively evacuating and filling with N_2 several times. The solvents [6 ml $(n\text{-}C_4H_9)_2O$ and 1 ml diglyme] were added in a counterstream of N_2. The reaction mixture was heated on an oil bath to 140°; throughout the reaction

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[*] Part LXXXIII, see ref. 1.

[**] Preliminary communication, see ref. 2.

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period, it was stirred slowly with a magnetic stirrer and a slow stream of N_2 was kept through the system. After about 4 h, the vessel was transferred to a large oil bath which had been preheated to 140° and was allowed to cool over a long period of time to room temperature. After standing at room temperature overnight, the vessel was cooled in an ice bath for 1 to 2 hours. Throughout this cooling period, a slight positive pressure of N_2 was maintained in the system. The reaction mixture was then filtered under N_2 on a fritted glass filter; care was taken not to break the large crystals of $C_{14}H_{10}Cr(CO)_3$ which are formed during the cooling process. The residue was washed with *n*-hexane and sucked dry on the water pump. The product, when thoroughly dry, is stable in air for some time, and the dark crystals of the product could be mechanically separated from the white starting materials. The yield was 53 mg, or 1.5 percent of the theory. (Found: C, 64.77; H, 3.55; Cr, 16.82; O, 15.27; mol. wt. osmometric in benzene, 336. $C_{17}H_{10}CrO_3$ calcd.: C, 64.97; H, 3.21; Cr, 16.55; O, 15.27 %; mol. wt., 314.) Evaporation of the combined filtrate and washings under N_2 yielded a residue which, after removal of $Cr(CO)_6$, anthracene, and a small amount of a yellow chromium-containing compound by high vacuum sublimation, weighed 19 mg and contained a considerable amount of crude product. Solution in benzene, filtration, and addition of *n*-hexane yielded, on cooling to 0° for several hours, a small amount of crystalline product which was, however, not completely pure.

Physical measurements

The infrared spectra were measured on KI discs with a Perkin-Elmer Model 21 instrument. The carbonyl stretching frequencies were also measured in cyclohexane solution. NMR spectra were obtained on C_6D_6 solutions with a Varian A-60 instrument. Dipole moments were measured at 25° on C_6H_6 solutions; results are given without taking atomic polarization into consideration and were calculated from experimental data by the method of Guggenheim[9].

RESULTS AND DISCUSSION

Anthracenechromium tricarbonyl forms dark crystals which show a greenish irridescence. It starts to decompose at 184°, and melts 189–192°. Prolonged heating at lower temperatures also leads to decomposition. It is somewhat soluble in benzene and toluene, less so in chloroform, and almost insoluble in *n*-hexane. It decomposes instantly in methanol or acetone. All solutions are deep purple in color. Heating of the toluene solution leads to an exchange reaction according to the equation:

$$C_{14}H_{10}Cr(CO)_3 + C_6H_5CH_3 \longrightarrow C_6H_5CH_3Cr(CO)_3 + C_{14}H_{10}$$

The benzene solution does not undergo such a reaction under the experimental conditions. The complex decomposes readily in any solution exposed to air.

Anthracene gives a proton NMR spectrum in dilute CCl_4 which consists of three lines at τ values of 1.26, 1.73 and 2.23 with intensity ratios of 2:4:4. Molten $C_{14}H_{10}$ gives τ values of 1.9, 2.5 and 2.8. The assignments of these lines are to the 9 and 10, the 1, 4, 5 and 8, and the 2, 3, 6 and 7 hydrogens respectively[10].* The $C_{14}H_{10}Cr(CO)_3$

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* Values given in ref. 10 are with reference to benzene and cyclohexane. The above τ values were calculated by using the chemical shift of benzene (7.37) and cyclohexane (1.43) relative to TMS[11].

spectrum in C_6D_6 shows 5 signals of approximately equal intensities at τ values of 2.85, 2.95, 3.35, 4.97, and 5.43 relative to an internal TMS standard. Use of the aromatic solvent C_6D_6 tends to shift all values up field. Because of these solvent and concentration effects, a direct comparison of the spectra of the ligand and the complex is not possible. It is nonetheless clear that the lines of the protons on one of the side rings have been shifted strongly up field to 4.97 and 5.43 and that the $Cr(CO)_3$ group must therefore be attached to one of the side rings of anthracene. If the group were attached to the middle ring, a spectrum consisting of only three signals of intensity ratios 2:4:4 with the 9,10 proton signal strongly shifted is to be expected. The complex therefore is assigned the structure shown, and the proton signals are assigned as given in Table 1.

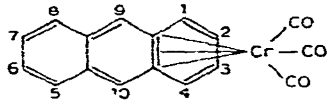

TABLE 1

PROTON NMR ASSIGNMENTS FOR ANTHRACENECHROMIUM TRICARBONYL

Measured in C_6D_6 relative to internal TMS standard.

τ	*Characteristics*	*Relative intensity*	*Assignment to protons*
2.85	broad singlet	2	9, 10
2.95	multiplet	2	5, 8
3.35	multiplet	2	6, 7
4.97	multiplet	2	1, 4
5.43	multiplet	2	2, 3

Anthracenechromium tricarbonyl has a dipole moment in benzene solution at 25° of 5.12 ± 0.06 D; this is very similar to that of the phenanthrene ($\mu = 5.03 \pm 0.08$ D)* and naphthalene ($\mu = 5.13 \pm 0.02$ D)[12] complexes. All condensed ring complexes have dipole moments somewhat greater than that of benzenechromium tricarbonyl[12] ($\mu = 4.96 \pm 0.05$ D).

The most prominent bands in the infrared spectrum of anthracenechromium tricarbonyl are given in Table 2 along with those of anthracene and 9,10-dihydroanthracenechromium tricarbonyl for comparison. From the similarity of the spectra of anthracene and anthracenechromium tricarbonyl, it is apparent that complex formation produces no great changes in the condensed ring system. The shifting to lower wave numbers of the frequencies associated with motions of the atoms near the $Cr(CO)_3$ entity is to be expected. The tentative frequency assignments listed in Table 2 are based on this and on the partial assignments for anthracene frequencies found in the literature[13,14]. The C–H stretching bands at 2841 cm^{-1} and 2933 cm^{-1} are most probably associated with the outer ring to which the metal atom is attached. The very strong band at 876 cm^{-1} is assigned to the C–H out-of-plane deformation of

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* Measurements by H. H. LINDNER.

TABLE 2

INFRARED SPECTRA OF ANTHRACENE, 9,10-DIHYDROANTHRACENECHROMIUM TRICARBONYL, AND ANTHRACENECHROMIUM TRICARBONYL

Only the main bands are given along with estimated intensities, vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad. ν = stretching frequency, ω_{CC} = carbon skeleton stretch, δ = in-plane deformation, γ = out-of-plane deformation.

Anthracene in KBr, cm^{-1}	*9,10-Dihydroanthracene-chromium tricarbonyl in KBr, cm^{-1}*	*Anthracenechromium tricarbonyl*		
		in KI, cm^{-1}	*in C_6H_{12} soln., cm^{-1}*	*Tentative assignment*
3012 s		3058 vw		ν_{CH}
2899 w		2933 vw		ν_{CH} Complexed outer-ring
2825 w		2841 vw		ν_{CH} Complexed outer-ring
	1954 vs	1949 vs	1982	ν_{CO}
		1859 sh	1924	ν_{CO}
	~ 1820, vs, br	1848 vs	1897	ν_{CO}
1779 m				
1618 s				
1531 m	1482 m	1508 w–m		ω_{CC}
1447 s	1453 s	1435 m–s		ω_{CC}
	1422 s	1372 s		ω_{CC}
1316 s		1302 s		ω_{CC}
1271 m	1274 m	1258 m		δ_{CH}
	1194 m			
1166 m	1182 m			
1146 s	1150 s	1139 s		δ_{CH}
998 s				
956 s	956 s	962 m–s		δ_{CH}
	909 s			
	893 m	884 m		
883 vs		876 vs		γ_{CH} Middle ring
	757 vs	757 m		γ_{CH} Complexed outer-ring
744 m–s		745 vs		γ_{CH} Non-complexed outer-ring
737 s	736 s			
725 vs		726 m		γ_{CH} Non-complexed outer-ring
	668 vs	665 vs		δ_{CO}
		615 s		δ_{CO}
		596 m–s		ν_{M-CO}
		524 s		δ_{CO}
		469 m		ν_{M-CO} or ν_{M-ring}
		456 s		

the middle ring; it is shifted slightly (from 883 cm^{-1}) from its position in free anthracene. Such a band does not appear in the spectrum of 9,10-dihydroanthracenechromium tricarbonyl. Finally, the splitting of the carbonyl stretching frequency at 1848 cm^{-1} in the solid state into two bands at 1924 cm^{-1} and 1897 cm^{-1} in cyclohexane solution indicates a low symmetry for the $Cr(CO)_3$ group. This is further indication that the site of binding of the metal is one of the outer rings of the anthracene molecule.

It is interesting to note that the iron tricarbonyl complex of anthracene has recently been shown also to contain a metal–terminal ring bond[15].

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SUMMARY

Anthracenechromium tricarbonyl has been prepared in pure crystalline form and its structure has been determined. The $Cr(CO)_3$ group is bound to the outer ring of the anthracene. Some of the properties of the complex are reported, and its infrared and proton NMR spectra are discussed.

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