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TRICARBONYLCHROMIUM COMPLEXES OF SOME SUBSTITUTED 9,10-DIHYDRO-9,10-*o*-BENZENOANTHRACENES*

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SUMMARY

Tricarbonylchromium complexes of 9,10-dihydro-1,4-dimethoxy-9,10-*o*-benzenoanthracene and 9,10-dihydro-1,4-dimethyl-9,10-*o*-benzenoanthracene have been prepared and characterized. Under the given experimental conditions, the dimethoxy ligand forms two isomeric complexes. These have been separated by both analytical and preparative scale liquid chromatography. Structures have been tentatively assigned on the basis of experiments with the NMR shift reagent $EuFod_3$. The methyl substituted ligand forms three isomeric complexes.

RESULTS AND DISCUSSION

The first metal complex of 9,10-dihydro-9,10-*o*-benzenoanthracene was recently reported[3]. In a continuation of this investigation, we have prepared tricarbonylchromium complexes of some ligands with substituents on this ring system and have observed in them an interesting type of isomerism.

Reaction of 9,10-dihydro-1,4-dimethoxy-9,10-*o*-benzenoanthracene with hexacarbonylchromium in refluxing diglyme or with triamminetricarbonylchromium in refluxing dioxane leads to the formation of the tricarbonylchromium complex of this ligand. The proton NMR spectral data for the ligand and the complex are summarized in Table 1. The upfield shift of the four proton AA′BB′ signal in the complex to τ4.67 from 2.83 ppm and the absence of an upfield shift in the two proton signal assigned to the methoxylated ring indicates that the tricarbonylchromium group is attached to a non-methoxylated aromatic ring. The most striking feature of the spectrum of the complex is that the signal assigned to the 2,3 protons appears as two peaks at τ3.40 and 3.50 ppm; similarly, the signal assigned to the methyl group appears as two peaks at τ6.17 and 6.22 ppm. The relative intensities of the signals are approximately the same in the case of the 2,3 protons as in the case of the methyl groups. This feature of

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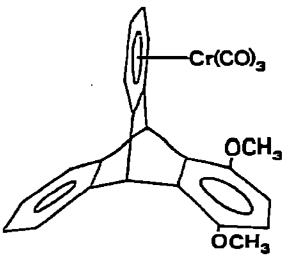
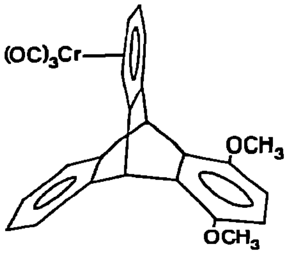
* The name "triptycene", originally proposed for this ring system[1] by Bartlett, *et al.*[2], is still in common use. Unfortunately, the numbering of the triptycene ring system[2] differs from that from which the systematic name is derived. The proper nomenclature of the complexes reported here presents more problems (*vide infra*). For these reasons, it seems wise to forego the obvious advantages of the trivial name and to use systematic names throughout this paper.

the spectrum is interpreted as indicating the presence in the sample of two isomers in which the $Cr(CO)_3$ group is attached to a non-methoxylated ring in ways that produce two different environments for the 2,3 protons and the methyl groups. Though the two non-methoxylated rings in the ligand are equivalent, the two sides of each ring are not equivalent: The structures (I) and (II) in which the $Cr(CO)_3$ groups are directed toward and away from the methoxylated ring respectively nicely account for the observations. Integration of the two peaks assigned to the 2,3 protons indicates that the mixture consists of 65% of one isomer and 35% of the other. Integration of the two methyl peaks is less precise, but is in substantial agreement with these results.



(I)



(II)

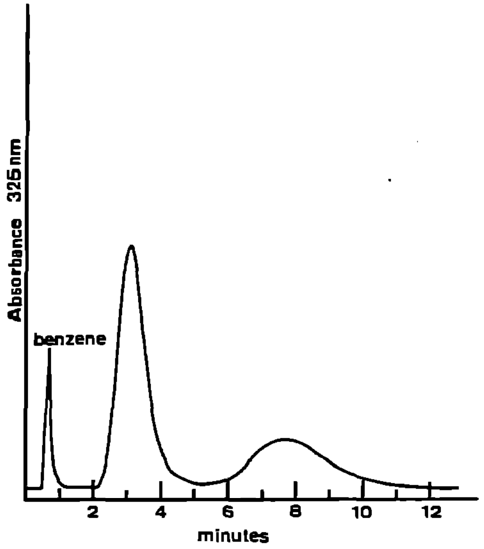
TABLE 1

PROTON NMR SPECTRA OF 9,10-DIHYDRO-1,4-DIMETHOXY-9,10-*o*-BENZENOANTHRACENE AND ITS TRICARBONYLCHROMIUM COMPLEX

	Chemical shift τ*(ppm)*[a]	*Assignment*
Ligand, $C_{22}H_{18}O_2$	2.83 (m)	8 aromatic protons[b]
	3.55 (s)	2 aromatic protons[c]
	4.12 (s)	2 bridgehead protons
	6.23 (s)	6 methyl protons
Complex, $C_{22}H_{18}O_2CR(CO)_3$	2.83 (m)	4 aromatic protons[b,d]
	3.40 (s) 3.50 (s)	2 aromatic protons[c,d]
	4.40 (s)	2 bridgehead protons
	4.67 (m)	4 aromatic protons[b,e]
	6.17 (s) 6.22 (s)	6 methyl protons

[a] s = Singlet, m = multiplet. All multiplets observed were of the AA'BB' type. τ values listed are centers of these multiplets. [b] Non-substituted ring. [c] Substituted ring. [d] Non-complexed ring. [e] Complexed ring.

It has recently been shown that the two isomers of tricarbonyl(2,3-dimethylnaphthalene)chromium can be separated and quantitatively determined by high speed column liquid chromatography[4]. This technique was used to investigate the isomer mixture described above. Elution of a sample of the complex dissolved in benzene from a 20 cm Carbowax 400/Corasil I column at 27° with the UV detector operated at 325 nm showed two well resolved peaks in addition to the solvent peak (Fig. 1). Separation was also achieved with a considerably shorter analysis time on a 20 cm



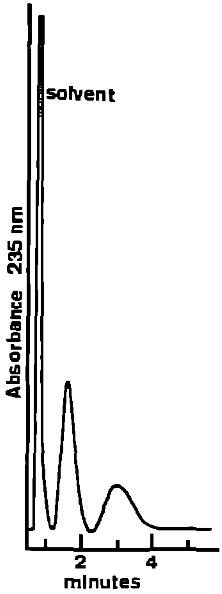


Fig. 1. Separation of the isomers of tricarbonyl[4b,5,6,7,8,8a-η-(9,10-dihydro-1,4-dimethoxy-9,10-*o*-benzenoanthracene)]chromium.
Column: 200 × 2.3 mm Carbowax 400/Corasil I. Temp., 27°. Sample size: ca. 50 μg.

Fig. 2. Separation of the isomers of tricarbonyl[4b,5,6,7,8,8a-η-(9,10-dihydro-1,4-dimethoxy-9,10-*o*-benzenoanthracene)]chromium.
Column: 200 × 2.3 mm Corasil I. Temp., 28°. Sample size: ca. 50 μg.

uncoated Corasil I column at 28° with the detector operated at 235 nm (Fig. 2). The capacity ratios of the two components on Carbowax 400/Corasil I at 27° were found to be 3.6 and 10.4 respectively. The relative abundance of the two isomers was obtained by measuring peak areas on ten chromatograms monitored at 325, 305, and 235 nm. Results ranged from 61.3 to 64.9 % of the predominant isomer, with an average value of 63.0 %. These results are in excellent agreement with those obtained by integration of the NMR peaks.

In a further experiment, a very concentrated solution of the isomer mixture in benzene was prepared. Samples of 20 μl volume were successively injected on the 20 cm Carbowax 400/Corasil I column at 27–28°. The effluent was monitored with the UV detector and was collected in four fractions: (1) benzene with the initial portion of the first component; (2) the major portion of the first component; (3) a mixed fraction of both components; and (4) the major portion of the second component. This process was repeated over a period of eight hours. Fractions (2) and (4) were each evaporated to dryness at room temperature, and the resulting solids were utilized for subsequent UV and NMR experiments.

UV spectra were recorded for 2,2,4-trimethylpentane solutions of fractions (2) and (4). These spectra were identical with each other and with the spectrum of a non-eluted sample of the complex. Solutions of fractions (2) and (4) were also injected separately on the chromatographic column. In each case, single peaks resulted whose individual retentions each corresponded to one of the two peaks observed for the mixed isomers. These experiments serve to identify the chromatographic peaks and to verify that no decomposition of the complexes occurred on the column.

The NMR spectra of fractions (2) and (4) were not of high quality because of the small amounts of material available. However, the spectrum of fraction (2) clearly shows a singlet at τ6.18 ppm while that of fraction (4) shows a singlet at τ6.23 ppm. These values agree very well with those reported in Table 1 for the methyl signals of the mixed isomers (τ6.17 and 6.22 ppm respectively). It is also in agreement with the observation that the major constituent is eluted first from the chromatographic column and is responsible for the downfield methyl signal in the NMR spectrum.

We have also succeeded in separating these isomers on a preparative scale chromatographic column. Separation was achieved by dissolving 200 mg of the crude reaction product in a minimal amount of benzene, and placing this solution on the column. Elution with a large amount of hexane (ca. 500 ml) removed unreacted starting material from the column, leaving the yellow product band at the top. Further elution with 25% ethyl ether in hexane resulted in collection of three yellow fractions: (A) the major portion of the first isomer; (B) a mixture of the two isomers; (C) the major portion of the second isomer (as indicated by TLC *versus* the original crude sample). After evaporation to dryness at room temperature, NMR spectra in $CDCl_3$ were recorded for each of these fractions. Fraction (A) exhibited a singlet at τ6.16 ppm ($-OCH_3$) and a singlet at τ3.41 ppm corresponding to the two aromatic protons on the substituted, uncomplexed ring. All peaks assigned to the second isomer were absent from this spectrum. The spectrum of fraction (C) was not of high quality because of the small amount of sample; however, two singlets at τ6.23 and 3.48 ppm were observed, corresponding to the methoxy group and the uncomplexed ring protons on the substituted ring of the second isomer respectively. These chemical

TABLE 2

PROTON NMR SPECTRA OF 9,10-DIHYDRO-1,4-DIMETHYL-9,10-*o*-BENZENOANTHRACENE AND ITS TRICARBONYLCHROMIUM COMPLEX[f]

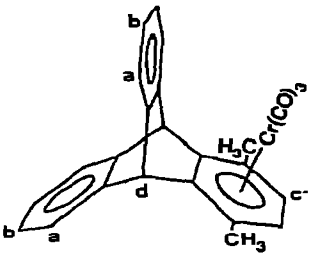
	Chemical shift τ*(ppm)*[a]	*Assignment*
Ligand, $C_{22}H_{18}$	2.84 (m)	8 aromatic protons[b]
	3.30 (s)	2 aromatic protons[c]
	4.37 (s)	2 bridgehead protons
	7.53 (s)	6 methyl protons
Complex, $C_{22}H_{18}Cr(CO)_3$	2.80 (m)	a and b protons[b,d], (III)–(V)
	3.19 (s) 3.28 (s)	c protons[c,d], (IV), (V)
	4.63 (s) 4.68 (s)	d protons, (III)–(V)
	4.67 (m)	a′ and b′ protons[b,e], (IV), (V)
	5.07 (s)	c′ protons[c,e], (III)
	7.52 (s) 7.58 (s) 7.64 (s)	methyl protons, (III)–(V)

[f] See footnotes to Table 1 for key to superscripts.

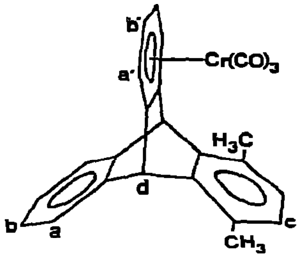
shifts are consistent with results obtained following LC separation of the complexes. The major isomer was again eluted from the column.

In an attempt to assign structures to the isomers, use has been made of the NMR shift reagent $EuFod_3$ recently reported[5]. The AA'BB' patterns in the spectra of the ligand and the complexes were unchanged on addition of $EuFod_3$. Addition of increasing amounts of $EuFod_3$ causes a gradual downfield shift of the methyl signals and of the 2,3 proton signals. The peaks of the minor constituent are shifted to a greater extent than are those of the major constituent. For example, at a mole fraction of $EuFod_3$/complex of 1.69, the methyl peak of the minor constituent is shifted from τ 6.22 to 5.37 ppm, while that of the major constituent moves from τ 6.17 to 5.65 ppm. The aromatic protons on the methoxylated ring are shifted in a similar manner (from τ 3.50 to 2.95 ppm and from τ 3.40 to 3.00 ppm respectively). The $Cr(CO)_3$ group in isomer (I) would probably interfere with complexation of $EuFod_3$ with the methoxyl groups more than would the $Cr(CO)_3$ group in isomer (II); therefore, the structure (I) is tentatively assigned to the predominant isomer. One would also expect that in isomer (I), the methyl signal would differ from that of the free ligand more than would the methyl signal of isomer (II). Though the differences are small and conclusions based on them at best tenuous, the data are in agreement with the assignment based on the $EuFod_3$ experiments.

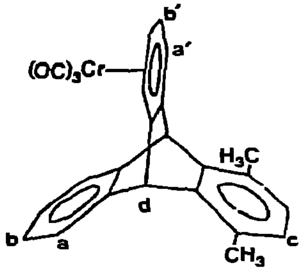
9,10-Dihydro-1,4-dimethyl-9,10-*o*-benzenoanthracene also forms a tricarbonylchromium complex. The proton NMR spectral data for this ligand and complex are summarized in Table 2. The spectrum of the complex indicates the presence of three isomers, (III)–(V). The 2,3 protons give three signals at τ3.19, 3.28 and 5.07 ppm.



(III)



(IV)



(V)

Similarly, there are three methyl signals observed at τ7.52, 7.58 and 7.64 ppm. Because of overlapping of the various signals, analysis of the spectrum is very difficult. The singlet at τ5.07 ppm can be assigned to the c' protons of structure (III); it is more intense than the singlets at τ3.19 and 3.28 ppm. Similarly, the methyl signal at τ7.64 ppm is more intense than the other two methyl signals, and can be assigned to the methyl groups of (III). A very approximate calculation from the integrated peaks shows the mixture to consist of about 50% isomer (III) and approximately equal amounts of isomers (IV) and (V).

It is interesting to note that, in the case of the methoxy substituted ligand, there is no evidence for complexation of the metal to the methoxylated ring, while in the case of the methyl substituted ligand the predominant isomer is the one with the metal attached to the methylated ring. Similar results have been observed with naphthalene derivatives[6]; 1,4-dimethoxynaphthalene forms a tricarbonylchromium complex in which the metal is bonded solely to the non-methoxylated ring, while 1,4-dimethylnaphthalene gives a mixture of two isomers.

Proper nomenclature for these complexes presents some interesting problems. Disregarding stereochemistry for the moment, the Chemical Abstracts name for compounds (I) and (II) is tricarbonyl[4b,5,6,7,8,8a-η-(9,10-dihydro-1,4-dimethoxy-9,10-*o*-benzenoanthracene)]chromium(0). Compound (III) is tricarbonyl-[1-4a(9a)-η-(9,10-dihydro-1,4-dimethyl-9,10-*o*-benzenoanthracene)]chromium(0), while compounds (IV) and (V) are named tricarbonyl[4b,5,6,7,8,8a-η-(9,10-dihydro-1,4-dimethyl-9,10-*o*-benzenoanthracene)]chromium(0). There is at present no generally accepted system for distinguishing stereoisomers such as (I) and (II), or (IV) and (V). It has been suggested[7] that the *endo–exo* system can be adapted to handle these isomers, even though it is usually applied to substituted bicyclo[*x*.*y*.*z*]alkanes rather than to coordination compounds or bridged fused ring systems. Nevertheless, if one defines the unsubstituted ring of the tricarbonyl[dimethoxy(or dimethyl)benzenoanthracene]-chromium compounds as the bridge, then *endo* and *exo* can be used to designate the tricarbonylchromium group as *trans* or *cis* to the "bridge". Compounds (I), (II), (IV) and (V) would then be, respectively, *endo*, *exo*, *endo*, and *exo*, these stereodescriptors being prefixed to the names given earlier.

EXPERIMENTAL

Proton NMR spectra were recorded on a Varian A-60A spectrometer, IR spectra on Perkin–Elmer Model 337 and Model 137 instruments, and UV spectra on a Cary 14 spectrophotometer. The liquid chromatograph was assembled from commercial and home-made parts. A high pressure Jeolco JLC-2A constant flow pump was used to pump the moving phase, spectral grade 2,2,4-trimethylpentane, through the column at 1.85 ml/min. Columns were constructed from precision-bore borosilicate tubing (20 cm × 2.3 mm i.d.) and were packed either with uncoated Corasil I, 37–50 μ, or with chemically bonded Carbowax-400 on 37–50 μ Corasil I. Both packings were obtained from Waters Associates, Inc. The columns were operated at 25–28°. Hamilton 701N and 705N syringes were used to inject samples through a silicone rubber septum into an injection chamber of minimal dead volume. A Carl Zeiss PMQ II spectrophotometer operated at 235, 305, or 325 nm and equipped with a Carl Zeiss microflow cell (volume 20 μl) was used as the detector. Chromatograms were recorded on a Simpson Model 2741 logarithmic recorder. Peak areas were measured with a planimeter.

Column chromatography for the macro separation of isomers (I) and (II) was carried out under a nitrogen atmosphere using a 1.5 × 30 cm neutral alumina column which had been packed in hexane. CAMAG neutral alumina was dried under vacuum for 3–4 days to remove water and residual oxygen, and was then deactivated with 5% (by weight) of nitrogen saturated distilled water before use. Hexane and benzene were purified by distillation from calcium hydride. Ethyl ether was predried over calcium chloride and then distilled from sodium-benzophenone.

The NMR shift reagent EuFod$_3$ was purchased from Pierce Chemical Co., Rockford, Ill. All other solvents were reagent grade, and were dried and saturated with N$_2$ before use. Analyses were by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

9,10-*Dihydro*-1,4-*dimethoxy*-9,10-*o*-*benzenoanthracene*[8]

This compound was prepared from 9,10-dihydro-1,4-dihydroxy-9,10-*o*-benzenoanthracene[2] by refluxing with methyl iodide in the presence of anhydrous potassium carbonate. M.p. 247–249°, (lit 239–241°)[8]. NMR in $CDCl_3$, see Table 1.

Tricarbonyl(9,10-*dihydro*-1,4-*dimethoxy*-9,10-*o*-*benzenoanthracene*)*chromium*(0)

Hexacarbonylchromium (2.0 g, 9.1 mmoles) and 9,10-dihydro-1,4-dimethoxy-9,10-*o*-benzenoanthracene (2.0 g, 6.4 mmoles) were heated in 10 ml diglyme under N_2 at 150° for 6 h. The reaction mixture was cooled, filtered through a medium glass frit, and the residue washed with petroleum ether (b.p. 30–60°). The combined filtrate and washings were chromatographed on a 1.3 × 20 cm silica gel column with 30–60° petroleum ether; if this is done very slowly, the yellow product band remains near the top of the column while unreacted starting materials are eluted. The yellow band was then eluted with chloroform, and an equal volume of 30–60° petroleum ether was added; after standing at −15° for 24 h, a yellow solid formed which was removed by filtration. Three recrystallizations from 1/2 chloroform/petroleum ether yielded 300 mg (11 %) of yellow crystals which were dried at 132° under vacuum. The crystals decomposed above 165° without melting. Elemental analysis of several samples has produced consistently good values for H and Cr and consistently low values for C. A typical analysis is the following: Found: C, 64.64; H, 3.94; Cr, 11.66. $C_{25}H_{18}CrO_5$ calcd.: C, 66.67; H, 4.03; Cr, 11.54 %. The mass spectrum shows peaks at 450 (molecular ion), 394 ($M-2CO$), 392 ($M-CO-2CH_3$), 366 ($M-3CO$), 351 ($M-3CO-CH_3$), 336 ($M-3CO-2CH_3$), and 314 $[M-Cr(CO)_3]$ as well as peaks assigned to ligand fragments. NMR in $CDCl_3$, see Table 1. Prominent IR bands (nujol mull) at 475 m, 533 s, 626 s, 665 s, 713 s, 737 m, 763 m, 782 m, 795 m, 832 m, 954 m, 1072 s, 1110 s, 1237 m, 1262 s, 1505 m, 1865 s, 1890 s, and 1950 s cm^{-1}.

This compound was also prepared by refluxing 1.57 g of the ligand (5.0 mmoles) and 1.0 g triamminetricarbonylchromium (5.4 mmoles) in 50 ml dioxane under N_2 for 5 h, according to the method of Rausch *et al.*[9]. The reaction mixture was cooled, filtered, and the filtrate evaporated to dryness. The solid was dissolved in tetrahydrofuran and placed on a 1.5 × 35 cm neutral alumina column (5 % H_2O) which had been packed in hexane. Elution with hexane removed all ligand, and the yellow band at the top was then removed with benzene. Evaporation of the benzene yielded a yellow solid which was recrystallized from 1/1 chloroform/hexane and vacuum dried at 30° for 24 h. Yield 350 mg (16 %).

Tricarbonyl(9,10-*dihydro*-1,4-*dimethyl*-9,10-*o*-*benzenoanthracene*)*chromium*(0)

Hexacarbonylchromium (2.0 g, 9.1 mmoles) and 9,10-dihydro-1,4-dimethyl-9,10-*o*-benzenoanthracene[10] (2.0 g, 7.1 mmoles) were heated in 8 ml n-butyl ether under N_2 at 140° for 56 h. The mixture was cooled, filtered, and the residue washed with hexane. Sublimation at 132° and 10^{-3} mmHg removed unreacted $Cr(CO)_6$ and ligand. The residue was dissolved in 30–60° petroleum ether and eluted very slowly through a 1.3 × 30 cm silica gel column using petroleum ether. When the yellow band reached the bottom of the column, it was removed with ethyl ether; the resulting solution was evaporated to ca. 20 ml, and cooled to −80°. The precipitated solid was removed by filtration and dried under vacuum at 132°. Yield 180 mg (6 %). The yellow crystals decomposed above 180° without melting. (Found: C, 71.57; H, 4.43; Cr. 12.49.

$C_{25}H_{18}CrO_3$ calcd.: C, 71.77; H, 4.34; Cr, 12.43%.) NMR in $CDCl_3$, see Table 2. Prominent IR bands (nujol mull) at 457 m, 533 s, 629 s, 645 m, 668 s, 713 s, 723 m, 742 m, 773 m, 809 m, 834 m, 1128 m, 1166 m, 1860 s, 1895 s, and 1910 s cm^{-1}.

ACKNOWLEDGEMENTS

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