

Preparation and Characterisation of 9,10-Dihydroanthracene and *tert*-Butyl-9,10-dihydroanthracene Complexes with One or Two Tricarbonylchromium Units; Crystal Structure of Tricarbonyl ($\eta^{1,2,3,4,4a,9a}$ -9,10-dihydroanthracene)chromium

Alan J. Whitton, Otto Kumberger, Gerhard Müller, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München,
Lichtenbergstraße 4, D-8046 Garching

Received February 16, 1990

Key Words: Dihydroanthracene / Dihydroanthracene, butyl-substituted / Tricarbonylchromium / Chromium complexes

The complexes [9,10-dihydroanthracene][tricarbonylchromium]_n [9,10-DHA][Cr(CO)₃]_n [*n* = 1 (**1**), 2 (**2**)] and the related mono- and bis(tricarbonylchromium) complexes of 2,6- and 2,7-di-*tert*-butyl-9,10-dihydroanthracene [2,6-DB-9,10-DHA][Cr(CO)₃]_n [*n* = 1 (**3**), 2 (**4**)] and [2,7-DB-9,10-DHA][Cr(CO)₃]_n [*n* = 1 (**5**), 2 (**6**)] have been prepared by heating the 9,10-DHA species in the presence of hexacarbonylchromium [Cr(CO)₆]. Evidence for the existence of the complex [2,6,9-tri-*tert*-butyl-9,10-DHA][Cr(CO)₃] (**7**) is also presented. The complexes have been characterised spectroscopically, and for complex **1** an

X-ray crystallographic structure determination has been carried out. This complex adopts the unexpected structure in which the non-coordinated arene ring is bent towards the Cr(CO)₃ moiety. The syntheses and spectroscopic characterisations of 2,6- and 2,7-di-*tert*-butylanthracene (2,6- and 2,7-DBA), 2,6- and 2,7-di-*tert*-butyl-9,10-dihydroanthracene (2,6- and 2,7-DB-9,10-DHA), 2,6,9-, 2,7,9- and 2,7,10-tri-*tert*-butyl-9,10-dihydroanthracene (2,6,9-, 2,7,9- and 2,7,10-TB-9,10-DHA), and 2,6,9,10- and 2,7,9,10-tetra-*tert*-butyl-9,10-dihydroanthracene (2,6,9,10- and 2,7,9,10-TeB-9,10-DHA) are also given.

The structures of 9,10-dihydroanthracene (9,10-DHA) and related species have been the subject of much interest in recent years¹⁻⁸. Three X-ray crystallographic determinations¹⁾ of 9,10-DHA have been carried out which consistently show that the central ring of the molecule is bent into a "boat" conformation with an angle between the planes of the arene rings of 144.7°^{1b)} (144.5°^{1c)}). Substitutions at C-9 and C-10 have been found to alter this angle as shown by the crystal structures of *cis*-9-ethyl-10-methyl-9,10-DHA (152°)²⁾, *trans*-9-isopropyl-10-methyl-9,10-DHA (128.7°)³⁾, and 9-*tert*-butyl-9,10-DHA⁵⁾.

Experimental⁶⁾ and theoretical⁷⁾ studies infer that, in the parent molecule, there is a low barrier to "boat"-planar-"boat" interconversion at the central ring. NMR studies⁸⁾ on 9-substituted and 9,10-disubstituted 9,10-DHA molecules have shown that, as the substituent size increases (H < Me < Et < *i*Pr < *t*Bu), the preference for the occupation of the pseudo-axial position is increased.

On the other hand, X-ray crystallographic studies on weak-interaction 1:2 complexes between 9,10-DHA and the π -acceptor molecules 1,3,5-trinitrobenzene^{1c)} and SbBr₃⁹⁾ have shown that in these species the 9,10-DHA molecule adopts a flattened structure.

The complexes formed between 9,10-DHA and more strongly bound transition metal groups have not been rigorously investigated. As arene ligands can be conveniently coordinated to the tricarbonylchromium moiety to form stable complexes¹⁰⁾, Cr(CO)₃ was chosen as the transition metal group. Crystal structures of 1:1 complexes of Cr(CO)₃ with anthracene¹¹⁾, phenanthrene¹²⁾, and 9,10-dihydrophenan-

threne¹³⁾ have been described, but although IR¹⁴⁾ and ¹H-NMR¹⁵⁾ data for [9,10-DHA][Cr(CO)₃] have been previously mentioned, no detailed synthetic or structural work have been carried out. A number of complexes formed between transition metals and 9,10-DHA are known^{15,16)}, but no structure determinations of these have been undertaken. It is also of interest that the complex Cr(anthracene)₂ reacts with MeOH or acetone to form Cr(9,10-DHA)₂¹⁵⁾ while it was reported¹⁴⁾ that Cr(CO)₃(anthracene) is instantly decomposed under similar conditions.

In this paper we describe the syntheses of a number of new 9,10-dihydroanthracene ligands and report on their reactions with Cr(CO)₆ to form [9,10-DHA][Cr(CO)₃]_n complexes (*n* = 1, 2).

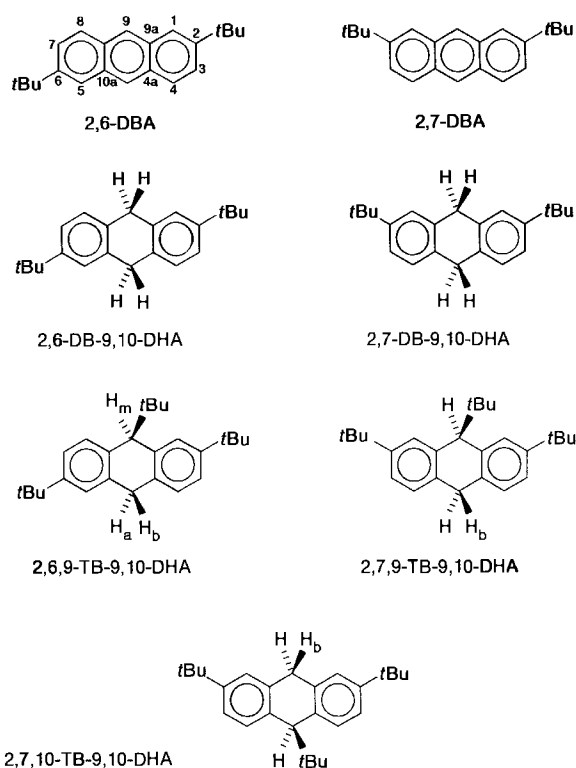
Preparation and NMR Data of 2,6- and 2,7-Di-*tert*-butyl-9,10-dihydroanthracenes and Related Compounds

The Friedel-Crafts reaction between 9,10-dihydroanthracene (9,10-DHA) and 2-chloro-2-methylpropane (*t*BuCl) in the presence of AlCl₃ gives a number of *tert*-butylated products. Fractional crystallisation from hexane yields 2,6-di-*tert*-butylanthracene (2,6-DBA)¹⁷⁾ as the major product. Further crystallisation from pentane solution affords 2,7-di-*tert*-butylanthracene (2,7-DBA). These compounds have been characterised by ¹H- (Table 1) and ¹³C- (Table 2) NMR, MS, IR, and physical data.

Both 2,6- and 2,7-DBA react in Na/NH₃(l) to form dark red-brown solutions which, on treatment with NH₄Cl(s), give the substituted 9,10-DHAs 2,6- and 2,7-di-*tert*-butyl-9,10-dihydroanthracene (2,6- and 2,7-DB-9,10-DHA). Com-

pounds 2,6- and 2,7-DBA also react with *tert*-butyllithium in THF solvent to give deep green-brown solutions which, on treatment with NH_4Cl , give 2,6,9-tri-*tert*-butyl-9,10-DHA (2,6,9-TB-9,10-DHA from 2,6-DBA) and 2,7,9- and 2,7,10-TB-9,10-DHA (from 2,7-DBA). As 2,6,9-TB-9,10-DHA is the only possible product obtained from 2,6-DBA it can be isolated cleanly, but the 2,7,9- and 2,7,10- isomers could not be separated by crystallisation or charge-transfer chromatography¹⁷. The relative ratio of 2,7,9- to 2,7,10-isomers is proposed to be approximately 1:2 as revealed by the ^1H - and ^{13}C -NMR spectra although assignment of the 2,7,10-substituted compound as the major isomer is based exclusively on the expected steric hindrance of the C-9 position as compared with the C-10 position. When the appropriate *tert*-butyllithiated intermediate is treated with *t*BuCl, the tetra-*tert*-butyl-9,10-DHA compounds 2,6,9,10- and 2,7,9,10-TB-9,10-DHA are formed as well as significant proportions of the tri-*tert*-butyl-substituted compounds. This is similar to the reported synthesis of 9,10-di-*tert*-butyl-9,10-DHA from anthracene in which significant proportions of 9-*tert*-butyl-9,10-DHA have also been obtained^{8b}.

Structural assignments are based primarily on ^1H - and ^{13}C -NMR data and by comparison with closely related compounds. Assignments of the aryl protons in the ^1H -NMR spectra of 2,6- and 2,7-DBA (Table 1) are facilitated by $^3J(\text{H}-\text{H})$ and $^4J(\text{H}-\text{H})$ couplings. Protons 9- and 10-H are easily characterised by their low-field shifts, and for the 2,7-isomer the two signals of 9- and 10-H are resolved. The ^1H -NMR spectra of the substituted 9,10-DHA molecules are likewise easily explained. The methylene protons of 2,7-DB-



9,10-DHA are observed as two singlets reflecting their inequivalent environments. In the spectra obtained for the 9-*tert*-butyl-substituted compounds, the assignment of the methylene protons can be made by a comparison with 9-*tert*-butyl-9,10-DHA^{8a}.

Table 1. ^1H -NMR data for 9,10-dihydroanthracenes

Compound	Solvent	Aryl protons δ (Hz)	9-, 10-H δ (Hz)	2,6,7-tBu	9,10-tBu
2,6-DBA	CDCl_3	4,8-H 7.91 d (8,8) 1,5-H 7.85 d (1.9) 3,7-H 7.53 dd (8.8, 1.9)	8.31 s 2H	1.42 s 18H	
2,6-DB-9,10-DHA	$[\text{D}_6]$ Acetone	7.36 s 2H 7.22 s 4H	3.88 s 4H	1.31 s 18H	
	CDCl_3	7.31 d (1.2) 2H 7.22 s (br) 4H	3.91	1.31 s 18H	
2,6,9-TB-9,10-DHA	CDCl_3	7.25 s 2H 7.18 s 4H	4.16 d (18.5) H_b 3.69 d (18.5) H_a 3.65 s H_m	1.31 s 18H	0.89 s 9H
2,6,9,10-TB-9,10-DHA	CDCl_3	1,5-H 7.44 d (1.9) 4,8-H 7.36 d (8.1) 3,7-H 7.09 dd (8.1, 1.9)	3.92 s 2H	1.30 s 18H	1.28 s 18H
2,7-DBA	CDCl_3	1,8-H 7.92 d (8.8)	8.33 (9-H)	1.45 s 18H	
		4,5-H 7.87 s (br)	8.30 (10-H)		
		3,6-H 7.54 dd (8.8, 1.8)			
2,7-DB-9,10-DHA	CDCl_3	7.29 s 2H	3.90 (9-H) 2H	1.30 s 18H	
		7.18 s 4H	3.84 (10-H) 2H		
2,7,9- and 2,7,10-TB-9,10-DHA	CDCl_3	7.24 s (br) 2H	4.20 d (18.2) H_b (minor)	1.30 s 18H	0.88 s 9H
		7.15 s (br) 4H	4.10 d (18.6) H_b (major)		
			3.70 complex individual peaks not resolved		
2,7,9,10-TB-9,10-DHA	CDCl_3	Signals not resolved in mixture	3.95 s (9-H) 3.98 s (10-H)	signals not resolved in mixture	

Table 2. ^{13}C -NMR data for 9,10-dihydroanthracenes (δ)

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-4a	C-10a	C-8a	C-9a	$\text{C}(\text{CH}_3)_3$			$\text{C}(\text{CH}_2)_3$				
															2,6,7	9,10	2,6,7	9,10	2,6,7	9,10		
Anthracene	127.9	125.1	125.1	127.9	122.9	125.1	125.1	127.9	126.0	126.0	131.5	131.5	131.5	131.5								
2,6-DBA	122.3	147.3	124.8	127.7	122.3	147.3	124.8	127.7	125.4	125.4	130.4	131.6	130.4	131.6	34.9	-		31.0	-			
2,7-DBA	122.2	147.4	124.5	127.8	127.8	124.5	147.4	122.2	<u>125.8</u>	<u>124.9*</u>	130.1	130.1	132.0	132.0	34.9	-		31.0	-			
Naphthalene																						
SCS effects ¹⁸⁾	-5.0	+22.7		-0.9	-0.2																	
9,10-DHA ⁷⁾	127.2	126.0	126.0	127.2	127.2	126.0	126.0	127.0	36.1	36.1	136.0	136.0	136.0	136.0	-	-	-	-	-	-	-	-
2,6-DB-9,19-DHA	123.0	149.0	124.4	127.1	123.0	149.0	124.4	127.1	36.1	36.1	134.0	136.5	134.0	136.5	34.5	-		31.6	-			
2,7-DB-9,10-DHA	123.0	148.8	124.3	127.1	127.1	124.3	148.8	123.0	<u>36.9</u>	<u>35.2*</u>	133.9	133.9	136.4	136.4	34.4	-		31.6	-			
9- <i>t</i> Bu-9,10-DHA (ref. 7)	<u>130.7</u>	<u>126.1</u>	<u>125.1</u>	<u>127.9</u>	<u>127.9</u>	<u>125.1</u>	<u>126.1</u>	<u>130.7</u>	57.5	37.2	<u>137.8</u>	<u>137.8</u>	<u>138.2</u>	<u>138.2</u>	-			39.1	-			28.1
2,6,9-TB-9,10-DHA	124.6	148.7	122.0	130.3	127.3	147.5	122.6	127.7	57.4	37.0	<u>135.2</u>	<u>137.7</u>	<u>134.6</u>	<u>137.2</u>	34.15	39.0	31.4	28.3				
2,7,9-TB-9,10-DHA	124.5	148.4	121.9	130.2	130.2	121.9	148.4	124.5	56.6	36.1	135.2	135.2	137.1	137.1	34.9	38.9	31.4	28.7				
2,7,10-TB-9,10-DHA	127.3	147.4	122.6	127.7	127.7	122.6	147.4	127.3	36.1	58.0	134.6	134.6	137.5	137.5	34.9	38.9	31.4	28.7				
2,6,9,10-TeB-9,10-DHA*	128.3	146.7	121.0	126.2	128.3	146.7	121.0	126.2	56.3	56.3	<u>138.8</u>	<u>141.4</u>	<u>138.8</u>	<u>141.4</u>	34.2	35.4	31.5	30.3				
2,7,9,10-TeB-9,10-DHA*	127.7	146.5	121.0	126.5	126.5	121.0	146.5	127.7	not clear	not clear	<u>138.7</u>	<u>138.7</u>	<u>141.0</u>	<u>141.0</u>				not clearly observed				30.2

* The arene carbon atoms for these compounds are arbitrarily assigned, or (underlined) assignment may be reversed.

Assignments of the ^{13}C -NMR spectra (Table 2) are less straightforward. For the compounds 2,6- and 2,7-DBA, the assignment of the C-9 and C-10 carbon resonances has been made by a comparison of the spectra for the two compounds in which one "doublet" carbon signal in the 2,6-DBA spectrum is split into two signals of half the relative intensity in the 2,7-DBA spectrum reflecting the inequivalence associated with 2,7-disubstitution.

The signals for the outer ring carbon atoms are assigned on the basis of the similarities between the naphthalene and anthracene systems. For 2-*tert*-butyl-7-fluoronaphthalene, 2-fluoronaphthalene, and related compounds, Kitching and co-workers¹⁸⁾ have introduced a table listing the substituent chemical shift (SCS) effects for *tert*-butyl substitution at the 2-position of naphthalene (Table 2). Application of this scheme to the 2-*tert*-butylanthracene systems (2,6- and 2,7-DBA) gives calculated chemical shifts very close to the experimentally determined values (Table 2).

For the substituted 9,10-DHA species, the methylene carbon resonances are assigned by a comparison with the parent molecule, and the aryl carbon atom resonances by applying the aforementioned SCS effects table¹⁸⁾.

As the concentrations of the 2,7,9- and 2,7,10-isomers are different, the intensity differences in the ^{13}C signals indicate which signals are associated with each arene ring. If it is assumed that the initially formed anion from the reaction of 2,7-DBA with *t*BuLi will, on steric grounds, preferentially have the butyl group in the C-10 position, and that protonation is nonselective, it can be proposed that the 2,7,10-TB-9,10-DHA is the major reaction product.

In the ^{13}C -NMR spectrum of 9-B-9,10-DHA (Table 2)⁷⁾ the resonances associated with the arene carbons C-1 to C-4 have not been unambiguously assigned. The proposal

that C-1 is perturbed less (+0.7 ppm) than C-4 (+3.5 ppm) and that the C-3 chemical shift moves by -0.9 ppm gives the most consistent calculated chemical shift positions compared with the observed shifts. Figure 1 shows the proposed

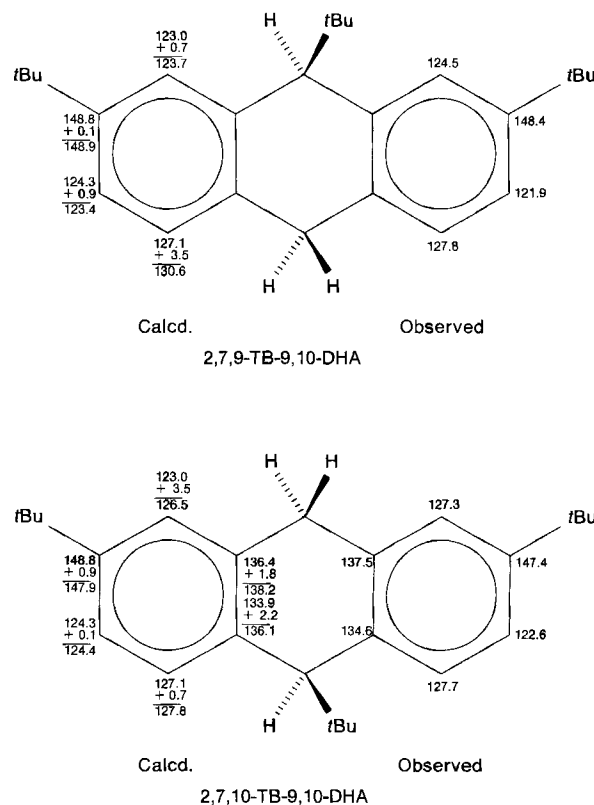


Figure 1. Observed and calculated chemical shifts for 2,7,9- and 2,7,10-TB-9,10-DHA

structures for the major and minor isomers from the *tert*-butylation of 2,7-DBA and the observed and calculated chemical shift values using the above convention. (The same results can be obtained if 2,7,9-TB-9,10-DHA is the major isomer and if the assignment convention is reversed.)

The most likely structure of the tri-*tert*-butyl-substituted compounds should be the bent structure similar to that found for 9-*tert*-butyl-9,10-DHA⁴⁾ in which the *tert*-butyl group attached to C-9 or C-10 occupies the pseudo-axial position (Figure 2).

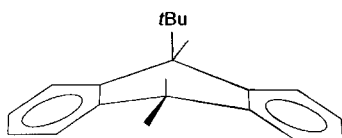


Figure 2. Proposed basic structure of 9-*tert*-butyl-substituted 9,10-DHAs

The tetra-*tert*-butyl compound 2,6,9,10-TeB-9,10-DHA can be isolated as colourless needle-shaped crystals and has been characterised by ¹H- and ¹³C-NMR, IR and physical properties. The isomer formed from 2,7-DBA, 2,7,9,10-TeB-9,10-DHA, has not been isolated cleanly but is observed as a minor component in a mixture with 2,7,9- and 2,7,10-TB-9,10-DHA.

The structures of the tetra-*tert*-butylated compounds have not been satisfactorily assigned. The ¹³C-NMR data of the *tert*-butyl group resonances of 2,6,9,10-TeB-9,10-DHA, when compared with *trans*- and *cis*-9-*tert*-butyl-10-ethyl-9,10-DHA, are more consistent with a *cis* arrangement of the substituents in the 9,10-positions, but a report on the synthesis of the related compound 9,10-DB-9,10-DHA suggests that only the *trans* isomer should be significantly formed in this reaction^{8b)}.

Preparation and Characterisation of [9,10-DHA][Cr(CO)₃]_n (n = 1, 2)

The reaction of 9,10-DHA, 2,6-DB-9,10-DHA, and 2,7-DB-9,10-DHA with Cr(CO)₆ in refluxing Bu₂O/THF solution¹⁹⁾ leads to the formation of compounds of the formula [9,10-DHA][Cr(CO)₃]_n (1, 2), [2,6-DB-9,10-DHA][Cr(CO)₃]_n (3, 4), and [2,7-DB-9,10-DHA][Cr(CO)₃]_n (5, 6). All complexes are yellow air-stable solids and have

[9,10-DHA][Cr(CO) ₃] _n	[2,6-DB-9,10-DHA][Cr(CO) ₃] _n
1: n = 1	3: n = 1
2: n = 2	4: n = 2
	[2,7-DB-9,10-DHA][Cr(CO) ₃] _n
	5: n = 1
	6: n = 2

Table 3. ¹H-NMR data for 9,10-dihydroanthracene-tricarbonylchromium complexes

Complex	Solvent	Free arene δ (Hz)	Coordinated arene δ (Hz)	Methylene (² J(H-H) Hz)	tBu
1 [9,10-DHA]- [Cr(CO) ₃]	CDCl ₃	7.24 s (br) 4H	1,4-H 5.38 2,3-H 5.30	AA'BB' H _a 3.94 d (16.8) H _e 3.59 d (16.8)	--
	[D ₆]Benzene	7.03 m 4H	1,4-H 4.57 2,3-H 4.50	AA'BB' 3.11 s 4H	--
2 [9,10-DHA]- [Cr(CO) ₃] ₂	[D ₆]Acetone	--	1,4,5,8-H 5.84 2,3,6,7-H 5.62	AA'BB' 3.94 s 4H	--
	[D ₆]Benzene	--	1,4,5,8-H 4.44 2,3,6,7-H 4.38	AA'BB' 2.75 s 4H	--
3 [2,6-DB-9,10- DHA][Cr(CO) ₃]	[D ₆]Acetone	5-H 7.32 s (br)	1-H 6.03 d (1.6)	H _e 3.92 m 2H	1.34 s 9H
		7-H 7.28 dd (8.8, 1.8)	3-H 5.82 dd (6.8, 1.6)	3.69 d 1H (17.4)	1.31 s 9H
		8-H 7.15 d (8.8)	4-H 5.62 d (6.8)	H _a 3.63 d 1H (17.6)	
4 [2,6-DB-9,10- DHA][Cr(CO) ₃] ₂	CDCl ₃	--	1,5-H 5.63 d (1.6)	3.68 s 4H	1.29 s 18H
		--	3,7-H 5.52 dd (6.8, 1.6)		
		--	4,8-H 5.32 d (6.8)		
5 [2,7-DB-9,10- DHA][Cr(CO) ₃]	[D ₆]Acetone	5-H 7.30 s (br)	1-H 5.98 s	H _e 3.81 d 2H (17.6)	1.34 s 9H
		6-H 7.26 d (7.8)	3-H 5.74 d (7.0)	H _a 3.70 d 1H (17.6)	1.31 s 9H
		8-H 7.18 d (7.8)	4-H 5.66 d (7.0)	H _a 3.68 d 1H (17.6)	
6 [2,7-DB-9,10- DHA][Cr(CO) ₃] ₂	[D ₆]Acetone	--	1,8-H 6.04 s	3.83 s 4H	1.32 s 18H
		--	3,6-H 4,8-H 5.78 s (br)		
7 [2,6,9-TB-9,10- DHA][Cr(CO) ₃]	[D ₆]Acetone	5,7,8-H 7.30 m	1-H 5.99 s	Major isomer	1.34 s 9H
			3-H 5.82 d (=6.6)	4.10 d (18.7) H _a	1.31 s 9H
			4-H 5.59 d (=6.6)	3.57 d (18.7) H _b 3.45 s H _m	0.96 s 9H
			Minor isomer		
				4.60 d (18.3) H _a	
				3.51 d (18.3) H _b	
				3.45 s H _m	

been characterised by ^1H - (Table 3) and ^{13}C - (Table 4) NMR, IR, and physical data. Also, an X-ray crystallographic study of **1** has been carried out.

The ^1H -NMR spectra (Table 3) of the monochromium complexes (**1**, **3**, **5**) in CDCl_3 or $[\text{D}_6]$ acetone each display resonances in three regions; at ca. $\delta = 7.2$, which are assigned to a free arene; at $\delta = 5.5\text{--}6.0$, corresponding to a coordinated arene group²⁰, and at $\delta = 3.5\text{--}4.2$ which are assigned to the methylene protons. Complexes **3** and **5** also exhibit two resonances at ca. $\delta = 1.3$ representing the inequivalent *tert*-butyl groups attached to the arene rings. The spectrum of **1** in $[\text{D}_6]$ benzene has been previously described¹⁵; it shows that the signals are significantly affected by the solvent. This may suggest some ordering of aromatic solvent molecules giving rise to anisotropic effects.

The assignment of the aryl protons for **3** is facilitated by the observed coupling constants in which one proton is represented by a doublet of doublets [$^3J(\text{H}\text{--}\text{H}) = \text{ca. } 8.8$ and $^4J(\text{H}\text{--}\text{H}) = 1.6$ Hz] with couplings to the other two. The signals of **5** are assigned by comparison with the spectrum of **3**. The aryl protons of **1**, both for the coordinated and free arenes, display second-order AA'BB' patterns.

The methylene protons of **1** are represented by two doublets [$^2J(\text{H}\text{--}\text{H}) = 16.8$ Hz]. The assignment of the pseudo-axial proton to that located at higher field is made by a comparison with the assignment of 9-*tert*-butyl-9,10-DHA^{8a}. The methylene proton regions in the spectra of complexes **3** and **5** are more complex as each proton is different in these species, and an exact assignment has not been made.

The ^{13}C -NMR spectra (Table 4) of **1**, **3**, and **5** confirm that one arene group is bound to a chromium as revealed by the signals at $\delta = 125\text{--}135$ representing the free arene, the signals attributable to the coordinated arene²¹ ($\delta = 90\text{--}110$), and by the resonances at ca. $\delta = 34$ attributable to the methylene carbons (C-9, C-10). The single carbonyl carbon resonances observed in the spectra of **1** and **5** at $\delta \approx 233$ indicate that the carbonyl ligands are rapidly interchanging at room temperature.

These data suggest that the most likely basic structure for complexes **1**, **3**, and **5** is that shown in Figure 3. However, these NMR data give no information concerning the bend-

ing angle at the methylene groups. In order to obtain more information on the bonding of 9,10-DHA in transition metal complexes, a single crystal of **1** suitable for X-ray analysis has been grown from Bu_2O solution. The molecular structure of **1** is shown in Figure 4, and bond lengths and angles are listed in Table 6. Non-hydrogen atom coordinates are given in Table 7.

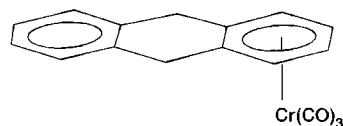


Figure 3. Proposed structure of mono(tricarbonylchromium) 9,10-dihydroanthracenes

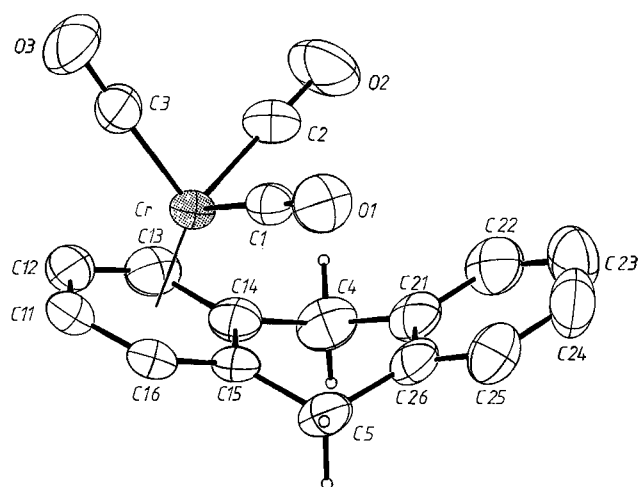


Figure 4. Molecular structure of [9,10-DHA][Cr(CO)₃] (**1**)

The compound **1** contains a tricarbonylchromium moiety centrally attached to one arene group of the 9,10-DHA ligand. The carbonyl ligands are staggered with respect to the C-C framework with one carbonyl directed away from the C14-C15 (C10a-C8a according to standard number-

Table 4. ^{13}C -NMR data for 9,10-dihydroanthracene-tricarbonylchromium complexes (δ)

Complex (solvent)	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-4a	C-10a	C-8a	C-9a	$\text{C}(\text{CH}_3)_2$		$\text{C}(\text{CH}_3)_3$	
															2,6,7	9,10	2,6,7	9,10
1 (CDCl_3)	92.7	91.3	91.3	92.7	127.4	126.8	126.8	127.4	34.3	34.3	107.9	133.3	133.3	107.9				
2 (C_6D_6)	92.6	91.4	91.4	92.6	92.6	91.4	91.4	92.6	*	*	*	*	*	*				
3 (CDCl_3)	90.5	119.4	91.0	92.6	127.0	124.5	149.6	123.7	34.8	34.8	*	*	*	*	34.8	-	31.4	-
																	31.2	-
5 (CDCl_3)	90.6	121.7	91.0	92.3	127.2	124.4	149.8	123.7	<u>34.9</u>	<u>33.5</u>	106.8	130.4	133.0	108.2	33.9	-	31.4	
									33.5	34.9							31.2	
7 (CD_3COCD_3)	96.7	*	94.8	92.3	<u>130.4</u>	<u>125.7</u>	149.0	123.8	56.1	36.5	<u>108.2</u>	<u>134.0</u>	<u>136.4</u>	<u>104.7</u>	34.2	40.2	31.7	28.6
					125.7	130.4					104.7	136.4	134.0	108.2			31.4	

* These carbon atoms are not observed or their assignments (underlined) may be reversed. CO signals were observed for **1** at $\delta = 232.8$ and for **5** at $\delta = 233.6$, but not for **2**, **3**, and **7**.

ing used in this paper) bond. The carbon-carbon distances in the coordinated arene ring are longer than in the free ring but are within the normal range found for (Arene)[Cr(CO)₃] complexes^{11–13}. The most significant feature of the molecule is that the non-coordinated arene moiety is bent towards the Cr(CO)₃ unit with a bending angle of 139.3°. This angle is more acute than that found for the free ligand (144.5°)^{1b}, and only *trans*-9-isopropyl-10-methyl-9,10-DHA³ has been demonstrated to have a more acute bending angle than **1**. The direction of bending is unexpected as it has been proposed¹⁵ that, in the related complex Cr(9,10-DHA)₂, the non-coordinated arene moiety would be bent away from the chromium atom.

The bis(tricarbonylchromium) complexes **2**, **4**, and **6** are less soluble (in benzene) than the monochromium complexes. The ¹H-NMR spectra, which display signals only in the coordinated arene region ($\delta = 5.5–6.0$), singlets in the methylene region, and singlets attributable to the *tert*-butyl groups (in **4** and **6**), infer that the chromium atoms are attached to different arene rings and to the opposite sides of the molecule (Figure 5). The assignment of the proton signals in the case of complex **4** is facilitated by the ³*J*(H–H) and ⁴*J*(H–H) coupling constants observed and is consistent with other 1,2-disubstituted arene Cr(CO)₃ complexes²⁰.

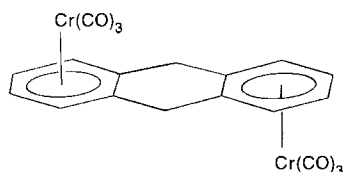


Figure 5. Proposed structure of bis(tricarbonylchromium) 9,10-dihydroanthracenes

The synthesis of Cr(CO)₃ complexes of 2,6,9-TB-9,10-DHA has also been attempted. The monochromium species can be readily prepared, but the two isomers formed (out of a possible four) cannot be separated and fully characterised. It is most likely that the tricarbonylchromium moiety is coordinated on the opposite side of the 9,10-DHA molecule (Figure 6) minimising the steric interactions between the *tert*-butyl and Cr(CO)₃ groups. This proposal is supported by the ¹³C-NMR spectrum in which the resonances assigned to the carbon atoms of the *tert*-butyl group at C-9 (at $\delta \approx 39$ and 28) are only slightly shifted on complexation. No evidence for the presence of a bischromium species has been obtained.

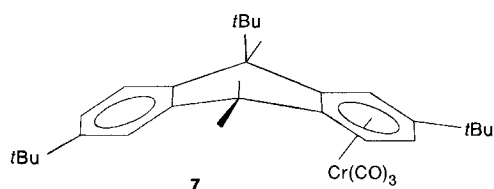


Figure 6. Proposed structure of [$\eta^{1,2,3,4,4a,9a}$ -2,6,9-TB-9,10-DHA]-[Cr(CO)₃] (**7**)

Attempts to use **1** as an arene with which to form weak interaction complexes with antimony trihalides (SbX₃, X = Cl, Br) have been unsuccessful as SbX₃ appears to attack the metal causing decomposition of the complex.

This work has been supported by the *Deutsche Forschungsgemeinschaft* and the *Royal Society* (European Science Exchange Fellowship Scheme) for A.J.W. Mr. J. Riede is thanked for acquiring the crystallographic data set.

Experimental

Unless otherwise specified, reactions were carried out in dried, degassed solvents. The NH₃(l)/Na(m) reactions were performed under dry, deoxygenated conditions, but subsequent workup was carried out in air with non-dried solvents. Reactions involving *t*BuLi were carried out in dried, degassed THF, but after protonation or *tert*-butylation the reaction mixtures were worked up in air. — NMR: Room temp.; Bruker WP 100 or Jeol GX 270 and GX 400 spectrometers; CDCl₃, [D₆]acetone, or [D₆]benzene, tetramethylsilane internal standard for all spectroscopic measurements. — IR: Nicolet 5DX FTIR spectrometer (resolution 4 cm⁻¹). Solid-state IR data of a number of the stronger absorptions are provided to characterise all solids obtained. — Microanalysis samples were subjected to high vacuum, often with gentle heating, for several hours prior to measurements.

2,6- and 2,7-Di-*tert*-butylantracene (2,6- and 2,7-DBA): The synthesis of these compounds was carried out in non-dried solvents in an open system. Aluminium trichloride (0.40 g, 3.0 mmol) was added to a suspension of 9,10-DHA (10.0 g, 55.4 mmol) in 2-chloro-2-methylpropane (33 ml) and CH₂Cl₂ (35 ml), and the mixture was refluxed. Immediately on heating, a yellow-orange colouration of the solvent occurred and an acidic gas (HCl) was evolved. After maintained at 60–70 °C for 22 h, the solution was cooled to room temp. and the solvent removed in vacuo to leave a brown solid. To this was added CH₂Cl₂ (50 ml) and the undissolved fraction collected and washed with hexane to yield crude 2,6-DBA (Yield: 7.46 g, 47%). The crude product was sufficiently pure for most purposes. The solvent was removed from the supernatant layer, and the residue was a light yellow oil which, when dissolved in hot pentane and allowed to cool to room temp., gave 2,7-DBA and a white solid (1.74 g, 11%). An NMR analysis suggested that the oil left after the second crystallisation included more 2,6- and 2,7-DBA and also some 2,6,9-TD-9,10-DHA (see later). These compounds could not be separated.

2,6-DBA could be purified by recrystallisation from hot hexane solution to give white (strongly UV-fluorescent) plates, m.p. 248 °C. — MS: *m/z* (%) = 290 [M⁺] (100), 291 (25), 292 (2.8), 275 [M⁺ – Me] (68.6), 276 (15.5), 277 (1.7), 260 [M⁺ – 2 Me] (9.2), 102 (14.5), 57 [Bu⁺] (23.6). — IR (KBr): $\tilde{\nu} = 2963$ cm⁻¹ vs, 2953 vs, 2901 s (sh), 2864 s, 1628 mw, 1474 m, 1458 m, 1364 ms, 1248 mw, 1167 mw, 935 w, 899 vs, 859 ms, 808 ms, 613 ms, 471 ms.

C₂₂H₂₆ (290.45) Calcd. C 90.98 H 9.02
Found C 90.90 H 8.85

2,7-DBA was purified by very slow concentration of a hexane solution to give long, thin colourless needles, m.p. 155 °C. — MS: *m/z* (%) = 290 [M⁺] (0.71), 291 (0.77), 292 (0.18), 275 [M⁺ – Me] (0.38), 179 [M⁺ – 2 Bu] (0.28), 86 [C₆H₇⁺] (17.0), 71 [C₅H₇⁺] (5.9), 57 [Bu⁺] (100). — IR (KBr): $\tilde{\nu} = 2957$ cm⁻¹ vs, 2907 s, 2901 s, 2867 s, 1475 mw, 1458 m, 1363 m, 905 ms, 897 ms, 804 m, 652 m, 469 m. — The ¹H-NMR spectrum of 2,7-DBA (Table 1) also displayed signals indicating ca. 0.33 mol equivalents of hexane in the

crystal lattice. The crystals become opaque when allowed to stand in the air suggesting solvent loss.

$C_{22}H_{26}$ (290.45) Calcd. C 90.98 H 9.02
Found C 90.31 H 9.67

2,6- and 2,7-Di-*tert*-butyl-9,10-dihydroanthracene (2,6- and 2,7-DB-9,10-DHA): 2,6-DBA (1.07 g, 3.7 mmol) [2,7-DBA (1.07 g, 3.7 mmol)] was added to a dried flask which was then flushed with pure, dry nitrogen. Dry ammonia (30 ml) was condensed into the flask using a dry ice/acetone cooling trap, and then sodium metal (0.21 g, 9.1 mmol) was added. The solution was stirred at reflux for 2 h which resulted in a dark red-brown solution. After this time, a large excess of NH_4Cl was added, discharging the colour and depositing a large amount of white compound on the side of the vessel. The NH_3 was allowed to evaporate at room temp., and final traces were removed in vacuo. The white solid was dissolved in CH_2Cl_2 (40 ml)/ H_2O (60 ml) to give two phases. The organic (lower) phase was separated and the aqueous phase washed twice with CH_2Cl_2 (20 ml), and the washings were added to the first fraction. The CH_2Cl_2 solution was dried with Na_2SO_4 . The solvent was removed in vacuo leaving a white impure solid.

In the 2,6-DBA preparation, recrystallisation from hot ethanol gave thin plates of 2,6-DB-9,10-DHA (0.5 g, 46%), m.p. 139 to 141°C. — MS: m/z (%) = 292 [M^+] (33.8), 293 (7.6), 294 (0.8), 277 [$M^+ - Me$] (42), 235 [$M^+ - Bu$] (73.9), 179 [$M^+ - (Bu + C_4H_8)$] (31.7), 57 [Bu^+] (100). — IR (KBr): $\tilde{\nu} = 2959\text{ cm}^{-1}$ vs, 2901 s, 2866 s, 1620 w, 1507 s, 1474 m, 1458 m, 1422 m, 1400 mw, 1362 m, 1337 w, 1266 mw, 1200 w, 1146 w, 964 w, 924 w, 916 w, 812 s, 725 mw, 606 m.

$C_{22}H_{28}$ (292.5) Calcd. C 90.35 H 9.65
Found C 90.23 H 9.30

In the 2,7-DBA reaction, recrystallisation from hot ethanol gave 2,7-DB-9,10-DHA as a white powder (0.93 g, 87%), m.p. 84 to 89°C. — IR: $\tilde{\nu} = 2952\text{ cm}^{-1}$ vs, 2930 s, 2865 s, 2808 m, 1611 mw, 1499 s, 1478 ms, 1460 ms, 1425 ms, 1407 w, 1392 w, 1362 w, 1271 ms, 1202 m, 1142 mw, 926 m, 606 w, 837 w, 846 s, 695 ms, 573 ms.

2,6,9-, 2,7,9-, and 2,7,10-Tri-*tert*-butyl-9,10-dihydroanthracene (2,6,9-, 2,7,9-, and 2,7,10-TB-9,10-DHA)

a) To a suspension of 2,6-DBA (0.62 g, 2.1 mmol) in THF (20 ml) was added a large excess of *t*BuLi and the mixture stirred for 20 min to give a dark-green solution. After this time, a large excess of NH_4Cl was added, and the solution was decoloured. The solution was then washed through silica gel with CH_2Cl_2 to remove LiCl and NH_4Cl . The solvent was removed in vacuo leaving a white oil which crystallised on standing to give a white solid, m.p. 120–130°C. Recrystallisation from pentane gave 2,6,9-TB-9,10-DHA as a white solid (0.67 g, 90%). A white powder could be obtained from EtOH solution, m.p. 140–143°C. — MS: m/z (%) = 348 [M^+] (0.075), 334 [$M^+ - CH_2$] (1.2), 291 [$M^+ - Bu$] (69.0), 235 [$M^+ - 2 Bu$] (82), 179 [$M^+ - 3 Bu$], (12.4), 57 [Bu^+] 100). $C_{26}H_{36}$ (348.6) Calcd. C 89.59 H 10.41
Found C 88.74 H 10.58

b) In an analogous reaction, *t*BuLi was treated with 2,7-DBA (0.20 g, 1.05 mmol) in THF to give a dark-green solution. After stirring at room temp. for 10 min, NH_4Cl was added and the colour was discharged. To the resultant solution was added CH_2Cl_2 (30 ml) and H_2O (40 ml) and the organic (lower) phase separated. The aqueous layer was washed twice with CH_2Cl_2 (20 ml), and the washings were united with the first fraction. The organic solution was dried with Na_2SO_4 before filtering. The solvent was removed in vacuo to yield a light yellow oil containing 2,7,9- and 2,7,10-TB-9,10-DHA.

These species could not be separated and were characterised as a mixture by 1H - and ^{13}C -NMR spectroscopy.

2,6,9,10- and 2,7,9,10-Tetra-*tert*-butyl-9,10-dihydroanthracene (2,6,9,10- and 2,7,9,10-TeB-9,10-DHA): Similar to the synthesis of the tri-*tert*-butylated compounds, the dark-green tri-*tert*-butyllithiated anionic intermediates were produced from 2,6-DBA (0.50 g, 2.6 mmol) [2,7-DBA (0.49 g, 2.6 mmol)] and *t*BuLi in THF. To these was added 2-chloro-2-methylpropane (*t*BuCl) which discharged the colours of the solutions. The solutions were treated with H_2O (40 ml) and CH_2Cl_2 (30 ml). Workup as in the case of 2,7,9- and 2,7,10-TB-9,10-DHA resulted, for both starting materials, in a light yellow oil containing a mixture of tri- and tetra-butylated species.

Recrystallisation of the 2,6,9,10-TeB-9,10-DHA/2,6,9-TB-9,10-DHA mixture gave clear, needle-shaped crystals of 2,6,9,10-TeB-9,10-DHA (0.30 g, 29%). (The mixture of the two compounds in the supernatant layer could not be separated.) M.p. 127–129°C. — MS: m/z (%) = 404 [M^+] (0.14), 402 [$M^+ - 2H$] (0.19), 348 [$M^+ - C_4H_8$] (18.5), 333 [$M^+ - (C_4H_8^+ Me)$] (3.9), 292 [$M^+ - 2 C_4H_8$] (56.9), 291 [$M^+ - (Bu + C_4H_8)$] (100), 290 [$M^+ - 2 Bu$] (32.9), 272 [$M^+ - (2 Bu + Me)$] (13.8), 235 [$M^+ - (2 Bu + C_4H_8)$] (50.9), 219 [$M^+ - (3 Bu + Me)$] (15.7), 179 [$M^+ - (3 Bu + C_4H_8)$] (39.6), 57 [Bu^+] (100). — IR (KBr): $\tilde{\nu} = 2959\text{ cm}^{-1}$ vs, 2904 s, 2875 s, 1610 mw, 1495 ms, 1480 ms, 1463 m, 1389 m, 1362 s, 1264 m, 1203 mw, 1172 mw, 823 m, 735 mw, 633 m.

$C_{30}H_{44}$ (404.7) Calcd. C 89.04 H 10.97
Found C 88.97 H 11.01

The other isomer, 2,7,9,10-TeB-9,10-DHA, could not be separated from the mixture containing 2,7,9- and 2,7,10-TB-9,10-DHA and was identified from the NMR spectra as a minor component (25–30%).

9,10-Dihydroanthracene Complexes of Tricarbonylchromium $\{[9,10-DHA][Cr(CO)_3]_n (n = 1, 2)\}$: In a standard synthesis, $Cr(CO)_6$ and the desired 9,10-DHA (quantities listed in Table 5) were placed in a round-bottomed flask fitted with a side arm and tap. Dibutyl ether and THF were added, and the solution was heated at 140°C (oil bath) for the desired time. The solution was cooled under N_2 and then the solvent removed by vacuum distillation. The products were dissolved in CH_2Cl_2 and the solution washed through a silica gel plug with CH_2Cl_2 to obtain mono- and some bis(tricarbonylchromium) products, and finally with acetone to get essentially pure bisproduct. The bischromium complexes 2, 4, and 6 were purified by washing with hexane. The monochromium complexes 1, 3, and 5 were purified either by recrystallisation from CH_2Cl_2 /hexane or by TLC on silica gel plates with CH_2Cl_2 /hexane (50:50) used as the eluent. Complex 7 was purified by TLC on silica gel plates with CH_2Cl_2 /hexane (50:50) eluant.

Mass spectra of these complexes generally displayed fragmentation patterns with significant peaks at m/z values corresponding to (i) for mono- $Cr(CO)_3$ complexes: M^+ , $M^+ - 2(CO)$, $M^+ - 3(CO)$ (often base peak), $M^+ - Cr(CO)_3$ and Cr^+ ($m/z = 52$); (ii) for bis- $Cr(CO)_3$ complexes: M^+ , $M^+ - 2(CO)$, $M^+ - 3(CO)$, $M^+ - 5(CO)$, $M^+ - 6(CO)$, $M^+ - Cr(CO)_5$, $M^+ - Cr(CO)_6$ (very strong), $M^+ - Cr_2(CO)_6$, and Cr^+ .

IR (KBr, cm^{-1}) of complexes 1–6: 1, $\nu(CO)$: 1959 vs (sh), 1954 vs, 1898 s, 1871 vs (sh), 1865 vs; $\delta(Cr-CO)$: 670 m, 634 m, 540 w, 530 w. 2, $\nu(CO)$: 1958 s, 1892 s, 1861 vs; $\delta(Cr-CO)$: 669 m, 631 m, 535 w. 3, $\nu(CO)$: 1940 vs, 1860 vs, 1846 s; $\delta(Cr-CO)$: 667 m, 632 m, 533 mw. 4, $\nu(CO)$: 1937 vs, 1871 vs; $\delta(Cr-CO)$: 667 m, 633 m, 534 m (br). 5, $\nu(CO)$: 1943 vs, 1872 s (sh), 1867 vs; $\delta(Cr-CO)$: 665 m, 631 m, 535 m. 6, $\nu(CO)$: 1952 vs, 1870 vs; $\delta(Cr-CO)$: 665 m, 629 m, 536 w.

Table 5. Experimental details

Complex	9,10-DHA (mmol)	Cr(CO) ₆ (mmol)	Bu ₂ O/ THF	Time [h]	Yield (%)	M.p. [°C] (dec.)	Calcd.		Found		M*	ν(CO) [cm ⁻¹]
							C	H	C	H		
1	1.86 g (10.3)	2.20 g (10.0)	50:10	24	2.7 g (85)	142 (180)	64.56	3.82	64.34	3.82	316	1976 s, 1909 s ^{b)}
2	0.225 g (1.25)	0.55 g (2.50)	25:5	68	0.50 g ^{a)} (88)	150 (175)	53.11	2.67	52.90	2.88	452	1966 s, 1890 s ^{c)}
3	0.130 g (0.44)	0.130 g (0.59)	10:3	18	0.14 g ^{a)} (75)	150 (180)	70.08 (67.14)	6.59 (6.37 ^{d)})	67.16	6.37	428	1969 s ^{e)} , 1905 s 1898 ^{b)}
4	0.25 g (0.86)	0.66 g (3.0)	25:5	72	0.37 g ^{a)} (76)	150 (210–215)	59.57 (61.68)	5.00 (5.18 ^{e)})	61.85	5.14	564	1959 vs., 1884 s ^{b)} ^{c)}
5	0.40 g (1.40)	1.05 g (4.80)	25:5	72	0.08 g ^{a)} (10)	147–148 (233)	70.08 (68.78)	6.59 (6.49 ^{f)})	68.78	6.55	428	1969 vs., 1904 s, 1989 ^{b)}
6	0.40 g (1.40)	1.05 g (4.80)	25:5	72	0.42 g ^{a)} (53)	147–148 (166–167)	59.57 (57.61)	5.00 (4.89 ^{g)})	57.65	4.97	564	1959 vs., 1882 s ^{b)} ^{c)}
[2,6,9-TB- 9,10-DHA]· Cr(CO) ₃	0.046 g	0.116 g	10:3	19		(oil)						1970 vs. 1897 s ^{b)}

^{a)} Decomposes without melting. — ^{b)} Hexane solution. — ^{c)} CH₂Cl₂ solution. — ^{d)} Calcd. with 0.28 equiv. of CH₂Cl₂ included. — ^{e)} Calcd. with 0.5 equiv. of C₆H₆ included. — ^{f)} Calcd. with 0.12 equiv. of CH₂Cl₂ included. — ^{g)} Calcd. with 0.3 equiv. of CH₂Cl₂ included.

Tricarbonyl(9,10-dihydroanthracene)chromium (1) and SbX₃ (X = Cl, Br): Complex 1 (60 mg, 0.19 mmol) and SbBr₃ (69 mg, 0.19 mmol) were dissolved in toluene (0.5 ml), and the solution was briefly heated. On cooling to -30°C no crystallisation occurred and on prolonged cooling a fine green precipitate formed which displayed no ν(CO) bands in the IR spectrum. Similar results were obtained for SbCl₃.

1 and 2,4,7-Trinitro-9H-fluoren-9-one (2,4,7-TNF): The result of heating 1 (145 mg, 0.46 mmol) and 2,4,7-TNF (0.46 mmol) in toluene (or CH₂Cl₂) was a brown colouration of the solution. Removal of the solvent gave a dark-brown oil which was insoluble in hexane. Redissolution in chlorobenzene and subsequent removal of the solvent gave a yellow solid which melted at ca. 60°C to reform the brown oil. The IR spectrum of the yellow solid indicated no complex formation. Strong heating of this oil resulted in the decomposition of this complex to afford a black insoluble fraction and a red, CH₂Cl₂-soluble fraction. The red fraction was dissolved in the minimum amount of hot CH₂Cl₂ and the solution then cooled to -30°C to yield (anthracene)·(2,4,7-TNF) as red crystals (identified by comparison with a sample prepared from anthracene and 2,4,7-TNF). — M.p. 187°C. — IR (KBr): $\tilde{\nu}$ = 1734 cm⁻¹ s, 1601 m, 1543 s, 1530 s, 1344 vs, 1311 mw, 1081 mw, 921 w, 914 w, 896 w, 839 w, 736 mw (sh), 731 m, 700 w, 471 w. [IR data of 2,4,7-TNF (KBr): $\tilde{\nu}$ = 1733 cm⁻¹ vs, 1617 ms, 1597 s, 1552 vs (sh), 1544 vs, 1520 vs, 1447 m, 1360 vs, 1345 vs, 1304 w, 1230 m, 1177 m, 1086 ms, 922 w, 858 w, 839 m, 790 w, 739 m, 730 ms, 698 mw.]

C₂₇H₁₅N₃O₇ (393.4) Calcd. C 65.72 H 3.06 N 5.51
Found C 65.58 H 3.14 N 5.39

9,10-Dihydroanthracene and 2,4,7-Trinitro-9H-fluoren-9-one: 9,10-DHA (180 mg, 1.0 mmol) and 2,4,7-TNF (1.0 mmol) were dissolved in CH₂Cl₂. After removal of the solvent in vacuo a bright yellow solid was obtained (no strong interaction is supposed to occur as the IR spectrum was very similar to that of free 2,4,7-TNF). This solid was heated strongly, and a red liquid was formed which on cooling gave a red solid. This was recrystallised from CH₂Cl₂ solution to yield red plate-shaped crystals of the formula (9,10-DHA)·(2,4,7-TNF). M.p. 100°C. — IR (KBr): $\tilde{\nu}$ = 1734 cm⁻¹ s, 1619 m, 1601 ms, 1545 vs, 1531 vs, 1480 w, 1487 w, 1448

m, 1423 w, 1345 vs, 1312 mw, 1224 w, 1176 w, 1080 m, 919 w, 904 w, 896 w, 848 w, 838 m, 788 w, 764 w, 738 s (sh), 732 s, 699 m.

C₂₇H₁₇N₃O₇ (495.5) Calcd. C 65.45 H 3.45 N 8.48
Found C 65.62 H 3.61 N 8.35

X-ray Structure Analysis of Tricarbonyl(9,10-dihydroanthracene)chromium (1): Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator, T = 23°C. Crystal size 0.25 × 0.30 × 0.25 mm. Crystal structure data: C₁₇H₁₂CrO₃, M_r = 316.279, a = 10.403(1), b = 13.193(2), c = 10.563(1) Å, β = 98.75(1)°, V = 1432.8 Å³, Z = 4, d_{calcd.} = 1.466 g/cm³, μ(Mo-K_α) = 7.8 cm⁻¹, F(000) = 648 e. The integrated intensities of 4368 reflections were measured up to (sin Θ/λ)_{max} = 0.615 Å⁻¹ by using Θ-2Θ scan techniques (Δω = 1.00 + 0.35 tan Θ, hkl range 12, ±16, ±12). Lp corrections and empirical absorption correction were applied to the intensity data. After merging of equivalent data (R_{int} = 0.016) 2726 unique structure factors remained, 2149 of which with F_o ≥ 4.0σ(F_o) were considered "observed" and used for all further calculations. The structure was solved by the Patterson methods (SHELXS-86) and refined

Table 6. Distances [Å] and angles [°] for tricarbonyl(9,10-dihydroanthracene)chromium (1) (esd's in units of the last significant figure in parentheses)

Cr -- C1	1.837(3)	Cr -- C2	1.832(3)
Cr -- C3	1.839(3)	Cr -- C11	2.218(2)
Cr -- C12	2.222(3)	Cr -- C13	2.209(2)
Cr -- C14	2.225(2)	Cr -- C15	2.227(2)
Cr -- C16	2.205(2)	O1 -- C1	1.153(3)
O2 -- C2	1.155(3)	O3 -- C3	1.153(3)
C11 -- C12	1.407(3)	C11 -- C16	1.384(4)
C12 -- C13	1.396(4)	C13 -- C14	1.414(4)
C14 -- C15	1.406(3)	C14 -- C4	1.519(4)
C15 -- C16	1.413(3)	C15 -- C5	1.509(3)
C4 -- C21	1.509(4)	C5 -- C26	1.511(4)
C21 -- C22	1.390(4)	C21 -- C26	1.398(3)
C23 -- C24	1.370(4)	C23 -- C22	1.371(4)
C24 -- C25	1.366(4)	C25 -- C26	1.387(4)
C1 -- Cr -- C2	87.7(1)	C1 -- Cr -- C3	92.0(1)
C2 -- Cr -- C3	89.1(1)	Cr -- C1 -- O1	176.9(2)
Cr -- C2 -- O2	178.3(3)	Cr -- C3 -- O3	178.7(3)
C14 -- C4 -- C21	112.5(2)	C15 -- C5 -- C26	112.0(2)

Table 7. Fractional atomic coordinates and equivalent isotropic thermal parameters for 1. $U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix (esd's in parentheses)

ATOM	X/A	Y/B	Z/C	U(eq.)
Cr	0.07976(4)	0.12094(3)	0.22308(3)	0.037
O1	0.2392(2)	0.3102(1)	0.2389(2)	0.055
O2	0.1968(2)	0.0681(2)	-0.0096(2)	0.101
O3	-0.1453(2)	0.2156(2)	0.0543(2)	0.095
C1	0.1747(3)	0.2387(2)	0.2314(2)	0.048
C2	0.1497(3)	0.0884(2)	0.0794(2)	0.055
C3	-0.0584(3)	0.1802(2)	0.1203(2)	0.050
C11	-0.0363(3)	0.0941(2)	0.3795(2)	0.053
C12	-0.0509(3)	0.0097(2)	0.2971(2)	0.046
C13	0.0591(3)	-0.0410(2)	0.2691(2)	0.048
C14	0.1850(3)	-0.0094(2)	0.3248(2)	0.052
C15	0.1995(3)	0.0749(2)	0.4070(2)	0.045
C16	0.0869(3)	0.1260(2)	0.4327(2)	0.049
C4	0.3076(3)	-0.0615(2)	0.2962(3)	0.068
C5	0.3348(3)	0.1082(2)	0.4637(2)	0.057
C21	0.4167(3)	0.0123(2)	0.2875(3)	0.067
C23	0.5981(4)	0.0706(3)	0.1923(3)	0.102
C24	0.6112(3)	0.1523(3)	0.2734(4)	0.084
C22	0.5014(4)	0.0009(2)	0.1987(3)	0.089
C25	0.5289(3)	0.1648(2)	0.3613(3)	0.073
C26	0.4303(3)	0.0956(2)	0.3704(2)	0.058

(SHELX76) to $R(R_w) = 0.034$ (0.027) for 190 refined parameters by using full matrix methods [non-hydrogen atoms anisotropic, hydrogen atoms constant with $U_{iso} = 0.05 \text{ \AA}^2$; all hydrogen atoms localized in difference maps; function minimized: $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$, $(\text{shift/error})_{\text{max}} = 0.001$ in final cycle], residual electron density $\Delta\rho_{\text{fin}}(\text{max/min}) = 0.20/-0.28 \text{ e/\AA}^3$. Table 6 lists selected distances and angles, Table 7 the atomic coordinates. Complete lists of atomic coordinates and observed and calculated structure factors have been deposited. These data may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54436, the names of the authors, and the journal citation.

CAS-Registry-Nummern

1: 12155-43-0 / 2: 111769-58-5 / 3: 128551-21-3 / 4: 128551-22-4 / 5: 128551-23-5 / 6: 128551-24-6 / 7 (isomer 1): 128551-25-7 / 7 (isomer 2): 128551-26-8 / 2,6-DBA: 62375-58-0 / 2,7-DBA: 99964-58-6 / 2,6-DB-9,10-DHA: 128575-84-8 / 2,7-DB-9,10-DHA: 128575-85-9 / 2,6,9-TB-9,10-DHA: 128551-16-6 / 2,7,9-TB-9,10-DHA:

128551-17-7 / 2,7,10-TB-9,10-DHA: 128551-18-8 / 2,6,9,10-TeB-9,10-DHA: 128551-19-9 / 2,7,9,10-TeB-9,10-DHA: 128551-20-2 / 2,4,7-TNF: 129-79-3 / 9,10-DHA: 613-31-0 / 9,10-DHA · 2,4,7-TNF: 128575-86-0 / anthracene · 2,4,7-TNF: 52898-84-7 / SbCl₃: 10025-91-9 / SbBr₃: 7789-61-9 / Cr(CO)₆: 13007-92-6 / 2-chloro-2-methylpropane: 507-20-0

- ¹⁾ ^{1a)} W. G. Ferrier, J. Iball, *Chem. Ind. (London)* **1954**, 1296. —
- ^{1b)} J. P. Reboul, G. Pepe, *Acta Cryst., Sect. C* **43** (1987) 537. —
- ^{1c)} F. J. Herbstein, M. Kapon, G. M. Reisner, *Acta Cryst., Sect. B* **42** (1986) 181.
- ²⁾ J. Bordner, R. H. Stanford Jr., H. E. Zieger, *Acta Cryst., Sect. B* **29** (1973) 313.
- ³⁾ R. H. Stanford Jr., *Acta Cryst., Sect. B* **29** (1973) 2849.
- ⁴⁾ T. Brennan, E. F. Putkey, M. Sundaralingham, *J. Chem. Soc., Chem. Commun.* **1971**, 1490.
- ⁵⁾ F. Leroy, C. Courseille, M. Daney, H. Bouas-Laurent, *Acta Cryst., Sect. B* **32** (1976) 2792.
- ⁶⁾ W. B. Smith, B. A. Shoulder, *J. Phys. Chem.* **69** (1965) 2022.
- ⁷⁾ P. W. Rabideau, J. L. Mooney, K. B. Lipkowski, *J. Am. Chem. Soc.* **108** (1986) 8130, and the references therein.
- ⁸⁾ ^{8a)} A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, A. L. Ternay Jr., *J. Am. Chem. Soc.* **92** (1970) 5912. — ^{8b)} P. P. Fu, R. G. Harvey, J. W. Paschal, P. W. Rabideau, *J. Am. Chem. Soc.* **97** (1975) 1145.
- ⁹⁾ H. Schmidbaur, R. Nowak, O. Steigelmann, G. Müller, *Chem. Ber.* **123** (1990) 1221.
- ¹⁰⁾ *Comprehensive Organometallic Chemistry* (G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds.) vol. 3, p. 1001, Pergamon Press, Oxford 1982.
- ¹¹⁾ F. Hanic, O. S. Mills, *J. Organomet. Chem.* **11** (1968) 151.
- ¹²⁾ K. W. Muir, G. Ferguson, A. G. Sims, *J. Chem. Soc. B* **1968**, 467.
- ¹³⁾ K. W. Muir, G. Ferguson, A. G. Sims, *J. Chem. Soc. B* **1968**, 476.
- ¹⁴⁾ B. R. Willeford Jr., E. O. Fischer, *J. Organomet. Chem.* **4** (1965) 109.
- ¹⁵⁾ C. Elschenbroich, R. Möckel, E. Bilger, *Z. Naturforsch., Teil B* **39** (1985) 375.
- ¹⁶⁾ ^{16a)} R. G. Sutherland, C. S. Chen, J. Pannekoek, C. C. Lee, *J. Organomet. Chem.* **101** (1975) 221. — ^{16b)} R. G. Sutherland, J. Pannekoek, C. C. Lee, *J. Organomet. Chem.* **129** (1977) C1. — ^{16c)} A. C. Sievert, E. L. Muetterties, *Inorg. Chem.* **20** (1981) 489.
- ¹⁷⁾ P. P. Fu, R. G. Harvey, *J. Org. Chem.* **42** (1977) 2407.
- ¹⁸⁾ M. Bullpitt, W. Kitching, W. Adcock, D. Doddrell, *J. Organomet. Chem.* **116** (1976) 161.
- ¹⁹⁾ C. A. L. Mahaffy, P. L. Pauson, *Inorg. Synth.* **19** (1978) 154.
- ²⁰⁾ F. van Meurs, J. M. Van der Toorn, H. van Bekkum, *J. Organomet. Chem.* **113** (1976) 341.
- ²¹⁾ L. A. Federov, P. V. Petrovski, E. I. Fedin, G. A. Panosyan, A. A. Tsoi, N. K. Baranetskaya, V. N. Setina, *J. Organomet. Chem.* **182** (1979) 499.

[68/90]