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Synthesis of (η^6-Arene)tricarbonylchromium Complexes: Regioselective Reaction of Chromium Hexacarbonyl with Polycyclic Aromatic Hydrocarbons[†]

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The reaction of chromium hexacarbonyl with 21 substituted polycyclic aromatic hydrocarbons (PAHs) was studied. The PAHs employed for study contain two to four aromatic benzo rings and include parent PAHs, mono- and dimethylated PAHs, PAHs with one or two rings saturated, and γ-keto-hexacyclic and phenyl-substituted derivatives. In general, a partially hydrogenated ring substituent, presumably due to its electron-donating character, directs the reaction regioselectivity to the substituted aromatic ring. This suggests that steric hindrance may not be as important a factor as electron-donating ability. Further evidence for this conclusion is that a methyl substituent, also having electron-donating character, exhibits a similar effect, whereas an electron-withdrawing keto functional group directs the reaction away from the substituted aromatic ring. On the basis of the electronic effects of the substituents observed in this study, we propose that total π-electron density, in terms of total π-bond order, of a benzenoid ring in a PAH is a decisive factor in determining the regioselectivity of the coordination reactions between PAHs and chromium hexacarbonyl. In contrast to previous reports that a $[Cr(CO)_3]$ group always bonds to the terminal aromatic ring of a PAH, we have found that reactions between chromium hexacarbonyl and two PAHs, 9-methylanthracene and 9,10-dimethylanthracene, occur on the central aromatic ring.

Introduction

Since the first (η^6-arene)tricarbonylchromium complex, (benzene)chromium tricarbonyl, was synthesized in 1957 by the reaction of chromium hexacarbonyl with benzene,[1] more than 150 (η^6-arene)tricarbonylchromium compounds derived from mono- and disubstituted benzene derivatives have been prepared.[2-19] The intense research in this field has occurred not only because of interest in the coordination chemistry but also on the basis of the utilization of organometallic complexes to conveniently synthesize compounds that cannot be obtained directly by organic reactions. Although coordination reactions with polycyclic aromatic hydrocarbons (PAHs) have been reported,[20-29] only the unsubstituted parent PAHs and disubstituted naphthalene have been studied.[4,21,22] In these studies, the coordination reaction took place on a terminal rather than a central ring of the parent PAH. The effect of electron-donating and electron-withdrawing substituents on the regioselectivity of the reaction between chromium hexacarbonyl and a substituted PAH has not been reported.

In this paper, we report the reaction of chromium hexacarbonyl with 21 substituted PAHs for the synthesis of the corresponding (η^6-arene)tricarbonylchromium complexes, as well as how the substituents affect the regioselectivity of the coordination reaction. The substituted PAHs are 2-methylanthracene (**1a**), 9-methylanthracene (**2a**), 9,10-dimethylanthracene (**3a**), 1-chloroanthracene (**4a**), 9-phenylanthracene (**5a**), 1-methylphenanthrene (**6a**), 2-methylphenanthrene (**7a**), 2-acetylphenanthrene (**8a**), 7-methylbenz[*a*]anthracene (**9a**), 11-methylbenz[*a*]anthracene (**10a**), 7,12-dimethylbenz[*a*]anthracene (**11a**), 1,2,3,4-tetrahydrophenanthrene (**12a**), 1,2,3,4-tetrahydrobenz[*a*]anthracene (**13a**), 8,9,10,11-tetrahydrobenz[*a*]anthracene (**14a**), 1,2,3,4-tetrahydrochrysene (**15a**), 7,8,9,10-tetrahydrobenzo[*a*]pyrene (**16a**), 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**17a**), 1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*e*]pyrene (**18a**), 4-keto-1,2,3,4-tetrahydrochrysene (**19a**), 11-keto-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**20a**), and 9-keto-1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*e*]pyrene (**21a**).

Experimental Section

General Procedures. All melting points were taken on a Yanagimoto capillary melting apparatus and are uncorrected. Infrared spectra were

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recorded on a Perkin-Elmer Model 883 spectrometer. Ultraviolet and visible absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Mass spectra were obtained using a JEOL JMS-DX300 spectrometer, with a solid probe inlet, by electron impact with a source temperature at 250 °C. Proton NMR spectra were obtained using a Bruker AM-500 in methylene chloride-d_2 except for **1a**–**5a** and **1b**–**5b**, which were run in acetone-d_6 on a JEOL Model 300 spectrometer. The chemical shifts are reported downfield from TMS (δ = 0.0 ppm).

Chemicals. Chromium hexacarbonyl, anthracene, phenanthrene, benz[*a*]anthracene, 2-methylanthracene (**1a**), 9-methylanthracene (**2a**), 9,10-dimethylanthracene (**3a**), 1-chloroanthracene (**4a**), 9-phenylanthracene (**5a**), 1-methylphenanthrene (**6a**), 2-methylphenanthrene (**7a**), 2-acetylphenanthrene (**8a**), 1-keto-1,2,3,4-tetrahydrophenanthrene, 7-keto-7,8,9,10-tetrahydrobenzo[*a*]pyrene, 7,12-dimethylbenz[*a*]anthracene (**11a**), 1-keto-1,2,3,4-tetrahydrobenz[*a*]anthracene, 11-keto-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**20a**), and 9-keto-1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*e*]pyrene (**21a**) were purchased from Aldrich Chemical Co., Milwaukee, WI. 7-Methylbenz[*a*]anthracene (**9a**) was prepared by nucleophilic aromatic substitution of 7-bromobenz[*a*]anthracene by phenyllithium followed by methyl iodide as described by Lee and Harvey.[30] 8,9,10,11-Tetrahydrobenz[*a*]anthracene (**14a**) was synthesized by hydrogenation of benz[*a*]anthracene catalyzed with Adam's catalyst (PtO_2).[31] 11-Methylbenz[*a*]anthracene (**10a**) was synthesized by Grignard reaction of 11-keto-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**20a**) with methylmagnesium bromide followed with acid-catalyzed dehydration and dehydrogenation.[32] 4-Keto-1,2,3,4-tetrahydrochrysene (**19a**) was prepared according to a published procedure.[33] 7,8,9,10-Tetrahydrobenzo[*a*]pyrene (**16a**) was prepared by Wolff–Kishner reduction of 7-keto-7,8,9,10-tetrahydrobenzo[*a*]pyrene with hydrazine and *tert*-butyl alcohol under reflux overnight followed by further reaction with potassium hydroxide.[34] 1,2,3,4-Tetrahydrophenanthrene (**12a**), 1,2,3,4-tetrahydrochrysene (**15a**), 1,2,3,4-tetrahydrobenz[*a*]anthracene (**13a**), 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**17a**), and 1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*a*]pyrene (**18a**) were similarly prepared starting with 1-keto-1,2,3,4-tetrahydrophenanthrene, 4-keto-1,2,3,4-tetrahydrochrysene (**19a**), 1-keto-1,2,3,4-tetrahydrobenz[*a*]anthracene, 11-keto-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**20a**), and 9-keto-1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*e*]pyrene (**21a**), respectively. All 21 starting materials, either purchased or synthesized, were characterized by comparison of their UV–visible absorption, mass, and proton NMR spectra with the published data. The proton NMR data for these compounds are shown in Table I.

General Procedure for Preparation of (η^6-Arene)tricarbonylchromium Complexes. The reactions of the PAHs and chromium hexacarbonyl were performed in refluxing dibutyl ether and tetrahydrofuran (THF) (5/1, v/v) under nitrogen for 2–24 h. Care was taken to exclude light to prevent photochemical decomposition of the resulting (η^6-arene)tricarbonylchromium complexes. Silica gel thin-layer chromatography was employed for monitoring the reactions. The products were first purified by recrystallization, followed by sublimation, resulting in the corresponding (η^6-arene)tricarbonylchromium complexes. The structural assignments of the products were based on the analysis of the UV–visible absorption, mass, IR, and proton NMR spectral data. The proton NMR spectral data of all the products are listed in Table I.

(η^6-2-Methylanthracene)tricarbonylchromium (1b). 2-Methylanthracene (**1a**) (96 mg, 0.50 mmol) and chromium hexacarbonyl (110 mg, 0.50 mmol) dissolved in 5 mL of dibutyl ether and 1 mL of THF were refluxed under nitrogen for 3 h. After filtration, the residue was recrystallized from hexane at −78 °C. The purplish crystals were further purified by sublimation, affording pure **1b** in 20% yield: mp 205–207 °C; IR (KBr) 1956 and 1885 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 380 (ϵ = 1550), 359 (ϵ = 1780), 257 (ϵ = 36 000), and 240 (ϵ = 20 900) nm; mass spectrum (75 eV) *m/z* 328 ([M]$^+$, 2), 272 ([M − 2CO]$^+$, 3), 244 ([M − 3CO]$^+$, 7), 192 ([M − Cr(CO)$_3$]$^+$, 100), and 52 ([Cr]$^+$, 17). Anal. Calcd for $C_{18}H_{12}O_3Cr$: C, 65.86; H, 3.68; O, 14.62. Found: C, 65.82; H, 3.70; O, 14.65.

(η^6-9-Methylanthracene)tricarbonylchromium (2b). Using conditions similar to those described for the synthesis of compound **1b**, product **2b** was obtained as purplish solid in 2% yield: mp 145–147 °C; IR (KBr) 1998 and 1942 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 365 (ϵ = 1800), 250 (ϵ = 28 000), and 240 (ϵ = 20 900) nm; mass spectrum (75 eV) *m/z* 328 ([M]$^+$, 5), 272 ([M − 2CO]$^+$, 5), 244 ([M − 3CO]$^+$, 35), 192 ([M − Cr(CO)$_3$]$^+$, 100), and 52 ([Cr]$^+$, 20). Anal. Calcd for $C_{18}H_{12}O_3Cr$: C, 65.86; H, 3.68; O, 14.62. Found: C, 65.80; H, 3.72; O, 14.68.

(η^6-9,10-Dimethylanthracene)tricarbonylchromium (3b). Using conditions similar to those described for **1b**, compound **3b** was obtained as purplish needles in 37% yield: mp 183–183 °C; IR (KBr) 1950, 1982, and 1864 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 350 (ϵ = 1780), 320 (ϵ = 1840), 288 (ϵ = 41 100), and 235 (ϵ = 20 400) nm; mass spectrum (75 eV) *m/z* 342 ([M]$^+$, 5), 286 ([M − 2CO]$^+$, 8), 258 ([M − 3CO]$^+$, 42), 206 ([M − Cr(CO)$_3$]$^+$, 100), and 52 ([Cr]$^+$, 68). Anal. Calcd for $C_{19}H_{14}O_3Cr$: C, 66.67; H, 4.12; O, 14.02. Found: C, 66.62; H, 4.12; O, 14.05.

(η^6-1-Chloroanthracene)tricarbonylchromium (4b). After reaction for 5.5 h, subsequent workup, and sublimation of the crude product, pure **4b** was obtained in 17% yield: mp 81–83 °C; IR (KBr) 1956 and 1842 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 326 (ϵ = 3530), 342 (ϵ = 3250) and 215 (ϵ = 41 000) nm; mass spectrum (75 eV) *m/z* 350 ([M]$^+$, 2), 266 ([M − 3CO]$^+$, 10), 212 ([M − Cr(CO)$_3$]$^+$, 52), and 52 ([Cr]$^+$, 100). Anal. Calcd for $C_{17}H_9ClO_3Cr$: C, 58.56; H, 2.60; O, 13.76. Found: C, 58.50; H, 2.63; O, 13.70.

(η^6-9-Phenylanthracene)tricarbonylchromium (5b). The reaction time was 5 h. After subsequent workup and sublimation of the crude product, pure purplish **5b** was obtained in 50% yield: mp 153–154 °C; IR (KBr) 1970 and 1860 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 316 (ϵ = 10 500), 251 (ϵ = 45 000) and 230 (ϵ = 44 000) nm; mass spectrum (75 eV) *m/z* 390 ([M]$^+$, 2), 334 ([M − 2CO]$^+$, 10), 306 ([M − 3CO]$^+$, 55), 254 ([M − Cr(CO)$_3$]$^+$, 82), and 52 ([Cr]$^+$, 100). Anal. Calcd for $C_{23}H_{14}O_3Cr$: C, 70.77; H, 3.61; O, 12.30. Found: C, 70.70; H, 3.66; O, 12.47.

(η^6-1-Methylphenanthrene)tricarbonylchromium (6b). After reaction for 2.5 h, subsequent workup, and recrystallization of the product, the purplish crystals of **6b** were obtained in 40% yield: mp 157–159 °C; IR (KBr) 1926 and 1860 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 357 (ϵ = 4200), 254 (ϵ = 25 000), and 226 (ϵ = 33 000) nm; mass spectrum (75 eV) *m/z* 328 ([M]$^+$, 5), 272 ([M − 2CO]$^+$, 8), 244 ([M − 3CO]$^+$, 38), 192 ([M − Cr(CO)$_3$]$^+$, 97), and 52 ([Cr]$^+$, 100). Anal. Calcd for $C_{18}H_{12}O_3Cr$: C, 65.86; H, 3.68; O, 14.62. Found: C, 65.80; H, 3.71; O, 14.66.

(η^6-2-Methylphenanthrene)tricarbonylchromium (7b). From 3.5 h of reaction and subsequent workup and sublimation, pure **7b** was formed in 28% yield: mp 157–159 °C; IR (KBr) 1947 and 1866 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 364 (ϵ = 8960), 216 (ϵ = 43 200), and 205 (ϵ = 40 900) nm; mass spectrum (75 eV) *m/z* 328 ([M]$^+$, 15), 272 ([M − 2CO]$^+$, 19), 244 ([M − 3CO]$^+$, 97), 192 ([M − Cr(CO)$_3$]$^+$, 14), and 52 ([Cr]$^+$, 100). Anal. Calcd for $C_{18}H_{12}O_3Cr$: C, 65.86; H, 3.68; O, 14.62. Found: C, 65.83; H, 3.71; O, 14.69.

(η^6-2-Acetylphenanthrene)tricarbonylchromium (8b). The reaction time was 5 h. Upon sublimation of the crude product, pure **8b** was obtained in 66% yield: mp 143–145 °C; IR (KBr) 1952 and 1865 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 365 (ϵ = 1700), 256 (ϵ = 11 000), and 213 (ϵ = 10 600) nm; mass spectrum (75 eV) *m/z* 356 ([M]$^+$, 4), 300 ([M − 2CO]$^+$, 8), 272 ([M − 3CO]$^+$, 34), 220 ([M − Cr(CO)$_3$]$^+$, 100), and 52 ([Cr]$^+$, 75). Anal. Calcd for $C_{19}H_{12}O_4Cr$: C, 64.05; H, 3.39; O, 17.96. Found: C, 64.00; H, 3.35; O, 18.02.

(η^6-7-Methylbenz[*a*]anthracene)tricarbonylchromium (9b). After reaction for 8 h and subsequent workup, pure **9b** was obtained as reddish bricks in 50% yield: mp 165–167 °C; IR (KBr) 1948 and 1874 (ν_{CO}) cm^{-1}; UV–visible (CH_2Cl_2) λ_{max} 358 (ϵ = 27 300), 255 (ϵ = 72 800), and 217 (ϵ = 72 000) nm; mass spectrum (75 eV) *m/z* 378 ([M]$^+$, 2), 322 ([M − 2CO]$^+$, 2), 294 ([M − 3CO]$^+$, 18), 242 ([M − Cr(CO)$_3$]$^+$, 16) and 52 ([Cr]$^+$, 100). Anal. Calcd for $C_{22}H_{14}O_3Cr$: C, 69.84; H, 3.73; O, 12.69. Found: C, 69.82; H, 3.71; O, 12.91.

(η^6-11-Methylbenz[*a*]anthracene)tricarbonylchromium (10b). After reaction for 8.5 h, the reaction mixture was recrystallized from toluene–hexane, affording pure **10b**, as reddish bricks in 40% yield: mp 165–167 °C; IR (KBr) 1952 and 1872 (ν_{CO}) cm^{-1}; UV–visible (CH_2Cl_2) λ_{max} 348 (ϵ = 1900), 265 (ϵ = 42 000), and 218 (ϵ = 22 000) nm; mass spectrum (75 eV) *m/z* 378 ([M]$^+$, 10), 322 ([M − 2CO]$^+$, 12), 294 ([M − 3CO]$^+$, 52), 242 ([M − Cr(CO)$_3$]$^+$, 100) and 52 ([Cr]$^+$, 67). Anal. Calcd for $C_{22}H_{14}O_3Cr$: C, 69.84; H, 3.73; O, 12.69. Found: C, 69.80; H, 3.70; O, 12.70.

(η^6-7,12-Dimethylbenz[*a*]anthracene)tricarbonylchromium (11b). After reaction for 7 h and subsequent workup and sublimation, pure **11b** was obtained as reddish bricks in 32% yield: mp 123–125 °C; IR (KBr) 1952, 1872, and 1865 (ν_{CO}) cm^{-1}; UV–visible (CH_2Cl_2) λ_{max} 364 (ϵ =

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Table I. Proton NMR Chemical Shifts (δ) and Assignments for (η^6-Arene)tricarbonylchromium Complexes in Methylene Chloride-d_2[a]

compd and Δδ	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11	H-12
1a*	7.81	3.11	7.46	8.02	7.98	7.46–7.52		7.81	8.18	8.32		
1b*	5.52	2.97	5.12	5.53	8.01	7.52–7.61		7.81	8.21	8.31		
Δδ	2.29	0.14	2.34	2.49								
2a*	8.00	7.46–7.52		8.33	8.33	7.46–7.52		8.00	3.11	8.33		
2b*	6.88	*7.43*	7.43	7.94	7.94	7.43	7.43	6.88	2.18	4.79		
Δδ	1.12			0.39	0.39			1.12	0.93	3.54		
3a*	7.62	7.35	7.35	7.62	7.62	7.35	7.35	7.62	3.11	3.11		
3b*	8.01	7.21	7.21	8.01	8.01	7.21	7.21	8.01	2.18	2.18		
Δδ	0.39			0.39	0.39			0.39	0.94	0.94		
4a*		7.83	8.41	8.41	8.41	7.83	7.83	8.41	9.18	8.90		
4b*		7.62–7.72		7.98	6.21	5.89	5.89	6.21	8.51	8.51		
Δδ					2.20	1.94	1.94	2.20	0.67	0.39		
5a*	7.68	7.40–7.50		8.02	8.02	7.40–7.50		7.68		8.51		
5b*	3.89	4.02–4.08		5.58	8.04	7.52–7.66		7.52		8.51		
Δδ	3.79	3.38–3.42		2.44								
6a	2.77	7.47	7.56	8.60	8.72	7.67	7.63	7.92	7.81	7.99		
6b	2.67	5.52	5.68	6.65	8.41	7.73	7.73	7.88	7.71	7.65		
Δδ	0.10	1.95	1.88	1.95	0.31					0.34		
7a	7.65	2.77	7.41	8.58	8.65	7.57	7.53	7.82	7.66	7.85		
7b	5.07	2.67	5.40	6.03	8.53	7.60–7.46		8.29	7.55	7.54		
Δδ	2.58	0.10	2.01	2.55	0.12					0.31		
8a	7.83	2.11	7.62	8.52	8.78	7.62	7.60	7.88	7.81	8.18		
8b	7.83	2.07	7.52	8.61	4.79	4.48	3.78	3.89	7.83	8.03		
Δδ					3.99	3.14	3.82	3.99		0.15		
9a	8.87	*7.56–7.74*		7.88	7.71	8.18	3.12	8.35	*7.56–7.74*		8.15	9.14
9b	6.86	*5.65*	*5.65*	6.05	7.29	8.05	3.05	8.33	*7.60–7.71*		8.14	8.77
Δδ	2.01	2.00	2.00	1.83	0.42							0.37
10a	8.90	7.62–7.78		7.88	7.72	7.84	8.32	7.91	7.62–7.78		3.10	9.31
10b	6.89	*5.70–5.60*		6.05	7.25	7.69	8.30	7.92	*7.46–7.57*		2.90	8.95
Δδ	2.01	2.05	2.05	1.83	0.47							0.46
11a	8.52	7.52–7.66		7.84	8.40	7.51	3.01	8.12	7.54–7.69		7.50	3.32
11b	6.75	5.55–5.64		5.01	7.18	7.89	2.98	*8.30, –8.42*	7.60–7.72		*8.30, –8.42*	3.32
Δδ	1.77	1.97–2.02		2.83								
12a	2.90	2.05	2.05	2.90	8.00	7.65	7.65	7.70	7.55	7.25		
12b	2.83	2.00	2.00	2.83	7.82	7.41–7.52		7.60	6.15	5.50		
Δδ									1.40	1.75		
13a	3.21	2.00	2.00	2.95	7.20	7.80	8.35	8.00	7.45	7.45	8.00	8.50
13b	3.15	1.90	1.90	2.90	5.60	6.40	8.15	7.85	7.40	7.40	7.85	8.30
Δδ					1.60	1.40	0.20					0.20
14a	8.65	7.65	7.65	7.67	7.87	7.55	7.60	3.05	1.95	1.95	3.05	8.40
14b	8.57	7.60	7.60	7.65	7.85	7.45	6.35	2.80	1.90	1.90	2.80	7.10
Δδ	0.08					0.10	1.25					1.30
15a	3.25	2.00	2.00	3.12	7.75	7.95	7.90	7.60	7.60	8.70	8.50	7.40
15b	3.00	1.90	1.90	2.85	7.70	7.85	7.75	7.60	7.60	8.40	6.65	5.50
Δδ										0.30	1.85	1.90
16a	8.15	8.10	8.12	8.15	8.13	8.25	3.28	2.05	2.14	3.45	8.30	8.17
16b	8.15	8.10	8.12	7.98	7.97	6.10	3.25	2.02	2.13	3.45	8.27	8.16
Δδ					0.16	2.15						
17a	7.61	*7.31*	*7.31*	7.22	1.94	1.82	7.90	2.90	2.70	2.70	2.90	8.10
17b	7.60	*7.30*	*7.30*	7.23	1.92	1.80	5.46	2.80	2.65	2.65	2.80	5.90
Δδ							2.44					2.20
18a	3.10	2.10	3.10	7.00	7.00	3.10	2.10	3.10	3.10	2.10	2.10	3.10
18b	2.70	1.80	2.70	6.80	6.80	2.70	1.80	2.70	2.70	1.80	1.80	2.70
Δδ	0.40	0.30	0.40	0.20	0.20	0.30	0.30	0.40	0.40	0.30	0.30	0.40
19a	3.26	2.24	7.85		8.85	8.70	8.50	7.50	7.60	9.30	9.20	8.00
19b	3.00	2.23	2.84		8.50	8.50	7.10	5.50	5.50	7.50	9.10	7.87
Δδ										0.30	1.85	1.90
20a	8.15	*7.35*	*7.35*	7.25	*2.65*	*2.65*	7.18	*2.65*	*2.65*	3.00	C=O	8.60
20b	6.03	5.56	5.40	5.48	*2.05–3.10*		7.17	*2.05–3.10*			C=O	8.27
Δδ	2.12	1.79	1.95	1.77								0.33
20c	7.69	*7.28–7.31*		7.22	*2.10–3.26*		5.36	*2.10–3.26*			C=O	6.80
Δδ	0.46						1.82					1.80
21a	3.10	2.10	3.10	7.00	7.15	3.10	2.10	3.10		2.50	2.10	3.10
21b	3.00	2.00	3.00	5.42	5.65	3.00	2.00	3.00		2.40	2.00	3.00
Δδ			1.58	1.50								

[a] An asterisk indicates compound measured in acetone-d_6.

6400), 293 (ϵ = 15 700), and 261 (ϵ = 16 000) nm; mass spectrum (75 eV) *m/z* 392 ([M]$^+$, 2), 336 ([M – 2CO]$^+$, 2), 308 ([M – 3CO]$^+$, 13), 256 ([M – Cr(CO)$_3$]$^+$, 100), and 52 ([Cr]$^+$, 16). Anal. Calcd for $C_{23}H_{16}O_3Cr$: C, 70.41; H, 4.11; O, 12.23. Found: C, 70.45; H, 4.15; O, 12.15.

(η^6-1,2,3,4-Tetrahydrophenanthrene)tricarbonylchromium (12b). The reaction mixture was refluxed under nitrogen for 5 h. After filtration, the residue was recrystallized from toluene–hexane at –78 °C, affording pure **12b** as orange crystals in 45% yield: mp 150–152 °C; IR (KBr) 1958 and 1886 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 420 (ϵ = 8600), 359 (ϵ = 12 500), and 210 (ϵ = 55 000) nm; mass spectrum (75 eV) *m/z* 318 ([M]$^+$, 5), 262 ([M – 2CO]$^+$, 7), 234 ([M – 3CO]$^+$, 32), 182 ([M – Cr(CO)$_3$]$^+$, 15), and 52 ([Cr]$^+$, 36). Anal. Calcd for $C_{17}H_{14}O_3Cr$: C, 64.15; H, 4.43; O, 15.08. Found: C, 64.20; H, 4.49; O, 15.00.

(η^6-1,2,3,4-Tetrahydrobenz[*a*]anthracene)tricarbonylchromium (13b). The reaction took place for 6 h. Upon sublimation of the resulting residue, pure **13b** was obtained as purplish solid in 45% yield: mp 205–207 °C; IR (KBr) 1986 and 1850 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 540 (ϵ = 4410), 380 (ϵ = 11 000), 359 (ϵ = 12 500), 343 (ϵ = 10 400), 251 (ϵ = 127 500), and 221 (ϵ = 29 000) nm; mass spectrum (75 eV) *m/z* 368 ([M]$^+$, 5), 312 ([M – 2CO]$^+$, 8), 284 ([M – 3CO]$^+$, 40), 232 ([M – Cr(CO)$_3$]$^+$, 100), and 52 ([Cr]$^+$, 55). Anal. Calcd for $C_{21}H_{16}O_3Cr$: C, 68.47; H, 4.38; O, 13.03. Found: C, 68.51; H, 4.41; O, 13.00.

(η^6-8,9,10,11-Tetrahydrobenz[*a*]anthracene)tricarbonylchromium (14b). The reaction took place for 3 h. After recrystallization of the crude product with toluene–hexane, compound **14b** was formed as orange needles in 40% yield: mp 195–195 °C; IR (KBr) 1955 and 1875 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 368 (ϵ = 3240), 339 (ϵ = 3350), 298 (ϵ = 6400), 255 (ϵ = 30 100), and 216 (ϵ = 28 600) nm; mass spectrum (75 eV) *m/z* 368 ([M]$^+$, 13), 312 ([M – 2CO]$^+$, 18), 284 ([M – 3CO]$^+$, 100), 232 ([M – Cr(CO)$_3$]$^+$, 8) and 52 ([Cr]$^+$, 60). Anal. Calcd for $C_{21}H_{16}O_3Cr$: C, 68.47; H, 4.38; O, 13.03. Found: C, 68.53; H, 4.42; O, 12.95.

(η^6-1,2,3,4-Tetrahydrochrysene)tricarbonylchromium (15b). The reaction time was 6 h. Upon recrystallization of the crude product with toluene–hexane, compound **15b** was obtained as yellowish needles in 55% yield: mp 192–194 °C; IR (KBr) 1970 and 1860 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 366 (ϵ = 15 000) and 218 (ϵ = 86 600) nm; mass spectrum (75 eV) *m/z* 368 ([M]$^+$, 10), 312 ([M – 2CO]$^+$, 15), 284 ([M – 3CO]$^+$, 95), 232 ([M – Cr(CO)$_3$]$^+$, 9), and 52 ([Cr]$^+$, 100). Anal. Calcd for $C_{21}H_{16}O_3Cr$: C, 68.47; H, 4.38; O, 13.03. Found: C, 68.46; H, 4.38; O, 13.05.

(η^6-7,8,9,10-Tetrahydrobenzo[*a*]pyrene)tricarbonylchromium (16b). The reaction took place for 6 h. After workup and recrystallization of the crude product with toluene–hexane, compound **16b** was obtained as orange crystals in 50% yield: mp 185–187 °C; IR (KBr) 1965 and 1870 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 345 (ϵ = 28 500), 328 (ϵ = 29 000), 313 (ϵ = 23 800), 279 (ϵ = 33 100), 267 (ϵ = 28 800), 246 (ϵ = 77 000), 238 (ϵ = 68 000), and 214 (ϵ = 60 900) nm; mass spectrum (75 eV) *m/z* 392 ([M]$^+$, 10), 336 ([M – 2CO]$^+$, 12), 308 ([M – 3CO]$^+$, 90), 256 ([M – Cr(CO)$_3$]$^+$, 70), and 52 ([Cr]$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_3Cr$: C, 69.71; H, 4.21; O, 12.52. Found: C, 69.69; H, 4.26; O, 12.78.

(η^6-5,6,8,9,10,11-Hexahydrobenz[*a*]anthracene)tricarbonylchromium (17b). The reaction proceeded for 6 h. Following the workup and sublimation, pure **17b** was obtained in 40% yield: mp 145–148 °C; IR (KBr) 1960 and 1880 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 329 (ϵ = 13 150), 259 (ϵ = 34 600), and 215 (ϵ = 60 400) nm; mass spectrum (75 eV) *m/z* 370 ([M]$^+$, 15), 314 ([M – 2CO]$^+$, 15), 286 ([M – 3CO]$^+$, 75), 234 ([M – Cr(CO)$_3$]$^+$, 10), and 52 ([Cr]$^+$, 80). Anal. Calcd for $C_{21}H_{18}O_3Cr$: C, 68.10; H, 4.90; O, 12.96. Found: C, 68.07; H, 4.93; O, 13.00.

(η^6-1,2,3,6,7,8,9,10,11,12-Decahydrobenzo[*e*]pyrene)tricarbonylchromium (18b). The reaction took place for 4 h. Upon recrystallization of the crude product from toluene–hexane, **18b** was formed as orange crystals in 50% yield: mp 146–148 °C; IR (KBr) 1970 and 1890 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 330 (ϵ = 4800), 273 (ϵ = 18 600), and 240 (ϵ = 40 600) nm; mass spectrum (75 eV) *m/z* 398 ([M]$^+$, 5), 342 ([M – 2CO]$^+$, 10), 314 ([M – 3CO]$^+$, 100), 262 ([M – Cr(CO)$_3$]$^+$, 28), and 52 ([Cr]$^+$, 48). Anal. Calcd for $C_{22}H_{22}O_3Cr$: C, 68.38; H, 5.73; O, 12.42. Found: C, 68.34; H, 5.70; O, 12.28.

(η^6-4-Keto-1,2,3,4-tetrahydrochrysene)tricarbonylchromium (19b). The reaction time was 3 h. Upon recrystallization of the residue from toluene–hexane, compound **19b** was obtained as orange needles in 25% yield: mp 173–175 °C; IR (KBr) 1980 and 1880 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 364 (ϵ = 9500) and 214 (ϵ = 63 000) nm; mass spectrum (75 eV) *m/z* 382 ([M]$^+$, 1), 326 ([M – 2CO]$^+$, 1), 298 ([M – 3CO]$^+$, 15), 246 ([M – Cr(CO)$_3$]$^+$, 60), and 52 ([Cr]$^+$, 15). Anal. Calcd for $C_{21}H_{14}O_4Cr$: C, 65.97; H, 3.69; O, 16.74. Found: C, 65.99; H, 3.72; O, 16.88.

(*A-ring*-η^6-11-Keto-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene)tricarbonylchromium (20b) and (*C-ring*-η^6-11-Keto-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene)tricarbonylchromium (20c). After reaction under reflux for 6 h, conventional workup, and recrystallization from toluene–hexane, compound **20b** was formed as a yellowish solid in 25% yield: mp 182–185 °C; IR (KBr) 1900 and 1790 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 329 (ϵ = 8110), 247 (ϵ = 34 600), and 218 (ϵ = 30 400) nm; mass spectrum (75 eV) *m/z* 385 ([M]$^+$, 10), 328 ([M – 2CO]$^+$, 11), 300 ([M – 3CO]$^+$, 65), 248 ([M – Cr(CO)$_3$]$^+$, 25), and 52 ([Cr]$^+$, 50). Anal. Calcd for $C_{21}H_{16}O_4Cr$: C, 65.62; H, 4.20; O, 16.65. Found: C, 65.60; H, 4.24; O, 16.70. A second product was obtained as orange solid in 10% yield from the filtrate upon sublimation followed by recrystallization from toluene–hexane: mp 196–198 °C; IR (KBr) 1920 and 1810 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 315 (ϵ = 6500), 240 (ϵ = 25 000), and 213 (ϵ = 25 000) nm; mass spectrum (75 eV) *m/z* 385 ([M]$^+$, 5), 328 ([M – 2CO]$^+$, 20), 300 ([M – 3CO]$^+$, 35), 248 ([M – Cr(CO)$_3$]$^+$, 90), and 52 ([Cr]$^+$, 70). Anal. Calcd for $C_{21}H_{16}O_4Cr$: C, 65.62; H, 4.20; O, 16.65. Found: C, 65.59; H, 4.22; O, 16.72.

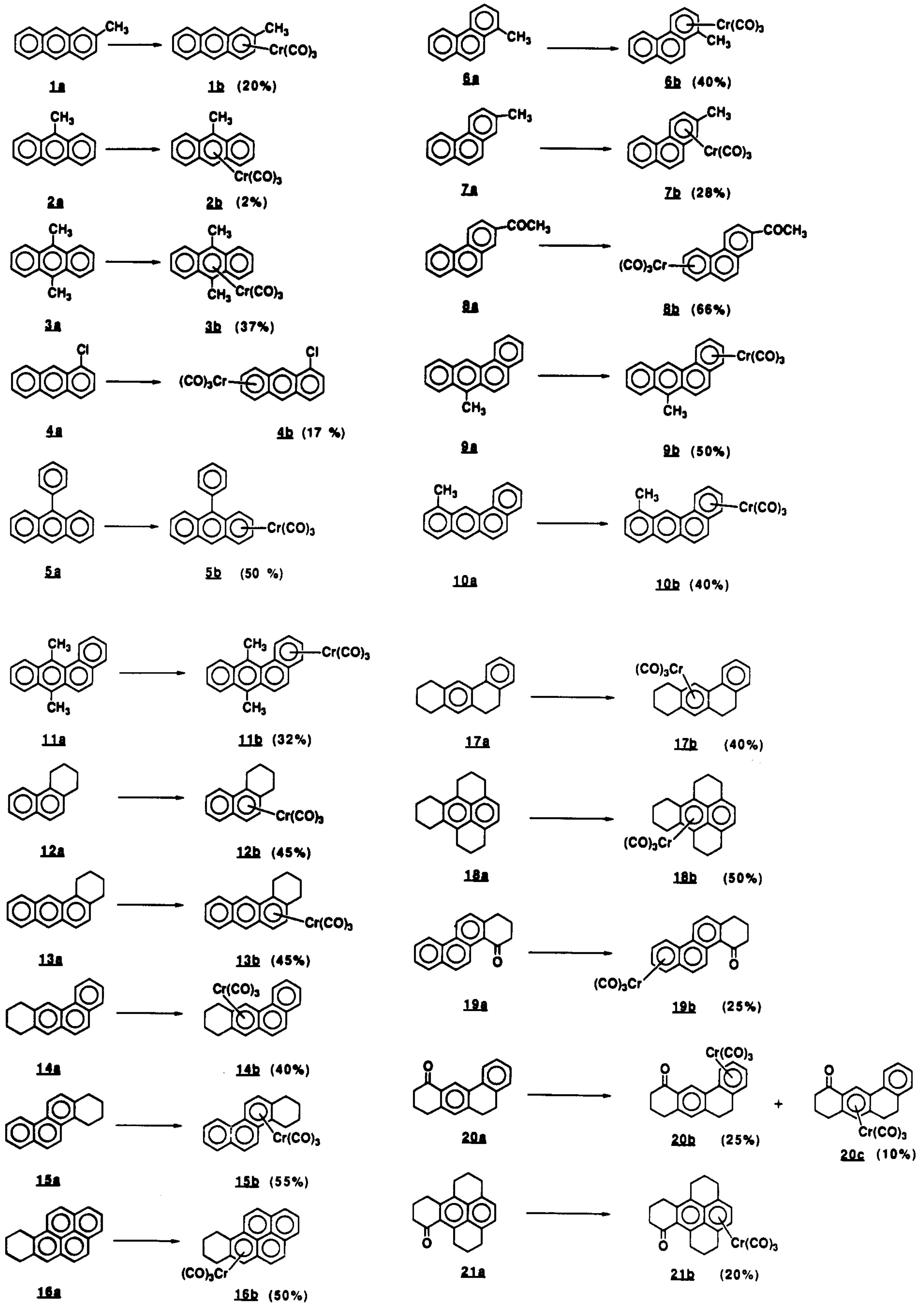
(η^6-9-Keto-1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*e*]pyrene)tricarbonyl chromium (21b). The reaction took place for 5 h. Sublimation of the crude product afforded product **21b** as a reddish solid in 20% yield: mp 146–148 °C; IR (KBr) 1980 and 1840 (ν_{CO}) cm^{-1}; UV–visible (MeOH) λ_{max} 235 (ϵ = 900), 340 (ϵ = 1500), and 210 (ϵ = 6550) nm; mass spectrum (75 eV) *m/z* 412 ([M]$^+$, 8), 356 ([M – 2CO]$^+$, 10), 328 ([M – 3CO]$^+$, 60), 276 ([M – Cr(CO)$_3$]$^+$, 100), and 136 ([Cr]$^+$, 36). Anal. Calcd for $C_{23}H_{20}O_4Cr$: C, 66.98; H, 4.89; O, 15.52. Found: C, 66.95; H, 4.92; O, 15.48.

Results

Preparation of (η^6-Arene)tricarbonylchromium Complexes. To explore the effect of a substituent on the regioselectivity of coordination reactions between chromium hexacarbonyl and PAHs, 21 substituted PAHs were chosen for study. These substituted PAHs, which contained two to four aromatic benzo rings, also contained either one or two methyl groups, a chloro atom, a phenyl group, an acetyl substituent, one or more partially hydrogenated rings, or a partially hydrogenated ring containing a keto group.

In general, the PAHs and chromium hexacarbonyl were reacted under reflux in dibutyl ether and tetrahydrofuran under an atmosphere of nitrogen for a period of 2–8 h. Care was taken to exclude light to prevent photochemical decomposition of the newly formed (η^6-arene)tricarbonylchromium complexes. The products were first purified by recrystallization, followed by sublimation and column chromatography over silica gel, resulting in the corresponding (η^6-arene)tricarbonylchromium complexes. The structural assignments of the products were based on the analysis of the UV–visible absorption, mass, IR, and proton NMR spectral data. The molecular ion was used to confirm formation of (η^6-arene)tricarbonylchromium complexes by mass spectrometry. The NMR spectral analysis of the products indicated that the Cr(CO)$_3$ moiety was attached to a specific aromatic ring. The proton NMR spectral data of all the products are listed in Table I. The structures of the PAH substrates and of the corresponding (η^6-arene)tricarbonylchromium complexes are shown in Scheme I. The reaction yields varied. The highest yield was that of (η^6-2-acetylphenanthrene)tricarbonylchromium (**8b**) (66%), followed by (η^6-1,2,3,4-tetrahydrochrysene)tricarbonylchromium (**15b**) (55%), (η^6-9-phenylanthracene)tricarbonylchromium (**5b**) (50%), (η^6-7-methylbenz[*a*]anthracene)tricarbonylchromium (**9b**) (50%), (η^6-1,2,3,4-tetrahydrobenzo[*a*]pyrene)tricarbonylchromium (**16**) (50%), and (η^6-1,2,3,6,7,8,9,10,11,12-decahydrobenzo[*e*]pyrene)tricarbonylchromium (**18b**) (50%). The lowest yield was found for (η^6-9-methylanthracene)tricarbonylchromium (**2b**) (2%), followed by (η^6-2-chloroanthracene)tricarbonylchromium (**4b**) (17%), and (η^6-2-methylanthracene)tricarbonylchromium (**1b**) (20%). The coordination was highly regioselective. With the exception of 11-keto-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**20a**), which

Scheme I. Structural Formulas of the PAH Substrates and the Structures and Yields of the (η^6-Arene)tricarbonylchromium Complexes Produced from the Reactions with $Cr(CO)_6$



resulted in two structural isomers, all the other reactions lead to only one (η^6-arene)tricarbonylchromium complex.

Reactions of anthracene and phenanthrene with chromium hexacarbonyl occur regioselectively at the terminal ring.[3,4,20,21] With an electron-donating methyl substituent, the reactions of 2-methylanthracene (**1a**), 1-methylphenanthrene (**6a**), and 2-methylphenanthrene (**7a**) with chromium hexacarbonyl occur preferentially at the methyl-substituted terminal ring. However, when the methyl group is not situated at a terminal ring, the methyl substituent directs the reactions of 9-methylanthracene (**2a**) and 9,10-dimethylanthracene (**3a**) regioselectively to the central aromatic ring. This finding is in contrast to the previous report that $Cr(CO)_3$ always bonded to a terminal rather than a central aromatic ring.[4] Nevertheless, the results of the reaction with 9-phenylanthracene (**5a**) indicate that a phenyl group at the C9 position of anthracene does not affect the regioselective preference for the terminal ring. This result may be explained in one of two ways. The steric hindrance of the phenyl substituent may affect regioselectivity, or the electronic effect of the phenyl substituent may be insufficient to shift the preference for coordination from the terminal ring.

The effect of a methyl group attached to the benz[*a*]anthracene molecule on the regioselectivity of the reaction is much less than that in methyl-substituted anthracenes. Thus, as the parent benz[*a*]anthracene, reactions of 7-methylbenz[*a*]anthracene (**9a**), 11-methylbenz[*a*]anthracene (**10a**), and 7,12-dimethylbenz[*a*]anthracene (**11a**) give exclusively the products with the tricarbonylchromium coordinated to the terminal benzo ring (the A-ring). These results indicate that the terminal benzo ring of benz[*a*]anthracene is strongly favored for six-electron (η^6) coordination with chromium.

The reaction of 2-acetylphenanthrene (**8a**) with chromium hexacarbonyl regioselectively occurs at the unsubstituted terminal ring. This was apparently the result of the mesomeric electron-withdrawing effect of the acetyl substituent. Reaction of 1-chloroanthracene (**4a**) occurs regioselectively at the unsubstituted terminal ring. The coordination of the terminal ring most remote from the electron-withdrawing chloro substituent occurred as a result of π-system extension via the chloro nonbonding electrons or chloro electron-withdrawing inductive effects. This retreat from the acetyl- and chloro-substituted rings may also be a result of the increased π-bond order associated with these substituents.

1,2,3,4-Tetrahydrophenanthrene (**12a**), 1,2,3,4-tetrahydrobenz[*a*]anthracene (**13a**), 8,9,10,11-tetrahydrobenz[*a*]anthracene (**14a**), 1,2,3,4-tetrahydrochrysene (**15a**), and 7,8,9,10-tetrahydrobenzo[*a*]pyrene (**16a**) contain a hydrogenated ring substituent attached to one of the two terminal benzo rings. These are the ideal compounds to explore the effect of a substituent, which can exhibit both an –I inductive effect and steric hindrance, on the coordination regioselectivity. The reactions of all these compounds occur exclusively at the substituted terminal ring. Compounds **17a** and **18a** are molecules with more than one saturated ring. Again, reactions took place on the more substituted terminal ring. These results suggest that a hydrogenated ring, presumably due to its electron-donating character, can direct the reaction regioselectively toward the most highly substituted aromatic ring system. Steric hindrance obviously did not play a significant role in this instance.

Compounds **19a**, **20a**, and **21a** contain an additional keto oxygen attached to the α-position of the compounds **15a**, **17a**, and **18a**, respectively. With such an electron-withdrawing group, reactions of these three compounds lead to the corresponding products **19b**, **20b** and **21b**, respectively, which have the tricarbonylchromium moiety situated away from the substituted terminal ring.

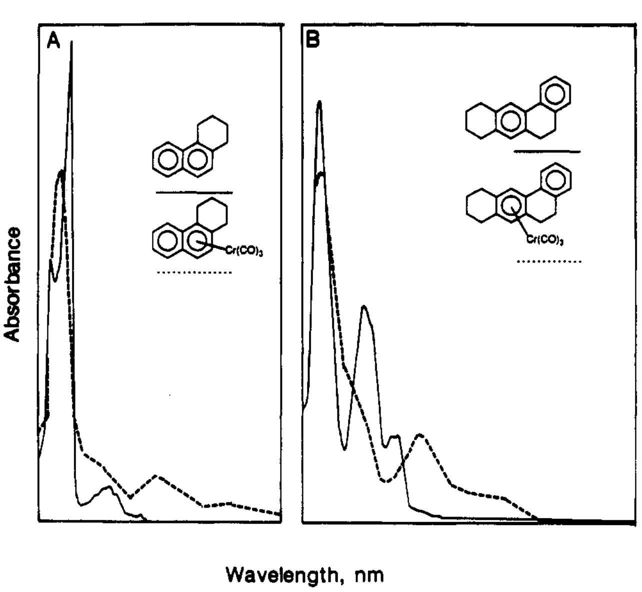


Figure 1. UV–visible absorption spectra of (A) 1,2,3,4-tetrahydrophenanthrene (**12a**) (—) and (η^6-1,2,3,4-tetrahydrophenanthrene)tricarbonylchromium (**12b**) (- - -) and (B) 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**17a**) (—) and (η^6-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene)tricarbonylchromium (**17b**) (- - -).

Spectral Analysis of (η^6-Arene)tricarbonylchromium Complexes. All the (η^6-arene)tricarbonylchromium complexes have similar IR spectra in the carbonyl region, showing two bands near 1960 and 1890 cm^{-1}. (η^6-Arene)tricarbonylchromium complexes are formed from the partial transfer of six π-electrons from a benzenoid ring of the PAH ligand to the chromium metal and the d-orbital electron back-donation from the metal to the ligand. As expected, the extended π–π conjugation of the PAH ligand resulted in the formation of visible absorptions at higher wavelength. Two examples are shown in Figure 1. In both cases, (η^6-1,2,3,4-tetrahydrophenanthrene)tricarbonylchromium (**12b**) (panel A of Figure 1) and (η^6-5,6,8,9,10,11-hexahydrobenz[*a*]anthracene)tricarbonylchromium (**17b**) (panel B of Figure 1) exhibited two absorptions at wavelengths higher than those of the corresponding parent PAHs.

The electron-impact mass spectra of all (η^6-arene)tricarbonylchromium complexes exhibited similar patterns with $[M - Cr(CO)_3]^+$ or Cr^+ as the base peak, $[M - 3CO]^+$ having moderate intensity, a very weak $[M - 2CO]^+$, and a weak molecular ion (see Experimental Section). This contrasts to the report that $[M - 3CO]^+$ or Cr^+ dominates the spectra measured with electron-impact ionization.[8]

The observed proton NMR chemical shifts and assignments for the (η^6-arene)tricarbonylchromium complexes are shown in Table I. The upfield change in the chemical shifts of the benzenoid ring that had been coordinated to the tricarbonylchromium moiety ranged up to 3.99 ppm. The magnitude of this shift is consistent with the work reported by others.[20] The aromatic protons on a neighboring aromatic ring were shifted upfield by 0.10–0.47 ppm, with one exception which exhibited a 1.12 ppm shift. The drastic change in the chemical shifts has enabled us to accurately determine which benzenoid ring of a PAH ligand is coordinated with the chromium tricarbonyl moiety (Scheme I). For example, the upfield shifts of the protons attached to the A-ring (consisting of C1, C2, C3, and C4) of compounds **9a**, **10a**, and **11a** are evidence that coordination occurs at the A-ring of these molecules. For illustration, the NMR spectra of **9a**,**b** are shown in Figure 2. The upfield shift of the methyl protons of compound **3a** clearly indicates that coordination occurs at the central ring (Table I and Scheme I). No significant change in the chemical shifts of all the protons was found for compound **18b** compared to those of compound **18a**. These results indicate that the chromium tricarbonyl moiety attaches to the protonless central ring of compound **18a**.

Discussion

In this study, we have shown that reactions of chromium hexacarbonyl with 21 substituted PAHs yield (η^6-arene)tricarbonylchromium complexes in a highly regioselective manner and that, evidenced by the proton NMR spectral analysis, the chromium atom of the (η^6-arene)tricarbonylchromium complexes coordinates to a benzenoid ring of the PAH molecule. With the only exception that reaction of 11-keto-5,6,8,9,10,11-hexabenz[*a*]anthracene (**20a**) results in two structural isomers, all other

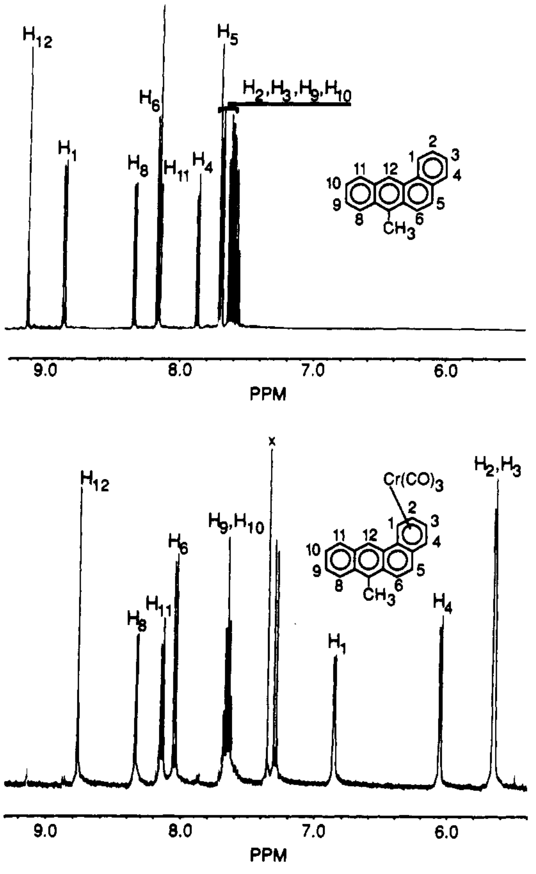


Figure 2. High-resolution 500-MHz proton NMR spectra of (A, top) 7-methylbenz[*a*]anthracene (**9a**) and (B, bottom) (η^6-7-methylbenz[*a*]anthracene)tricarbonylchromium (**9b**).

reactions form only one (η^6-arene)tricarbonylchromium product. Our results have also provided evidence regarding the effect of substituents on the regioselectivity of the reaction. Electron-donating substituents such as a partially hydrogenated ring or a methyl group enhance the reaction regioselectively at the substituted aromatic ring, and steric hindrance may not be an important factor. On the other hand, an electron-withdrawing substituent (e.g., the keto group) directs the reaction away from the substituted aromatic ring. On the basis of the electronic effects of the substituents observed in this study, we propose that total π-electron density of a benzenoid ring in a PAH is the most decisive factor in determining the regioselectivity of the coordination reactions between PAHs and chromium hexacarbonyl. Theoretically, total π-electron density of a benzenoid moiety can be represented by the sum of all six π-bond orders for that ring system. Thus, chromium hexacarbonyl regioselectively reacts with the benzenoid moiety of a PAH with the highest π-electron density or, in other terms, with the highest total π-bond order. On the basis of the published π-bond orders of the parent PAHs, including benzene, biphenyl, naphthalene, anthracene, phenanthrene, pyrene, and benz[*a*]anthracene, obtained by the simple LCAO–MO method,[35,36] the total π-electron bond orders of a benzenoid ring of each PAH have been calculated (Figure 3). Benz[*a*]anthracene, anthracene, phenanthrene, and pyrene all contain unique benzenoid rings with different total π-bond orders (Figure 3). In order of decreasing total π-bond order of a benzenoid ring, the values are benzene (4.002), biphenyl (3.912), the A-ring of benz[*a*]anthracene (3.747), the terminal ring of phenanthrene (3.737), naphthalene (3.681), the terminal ring of anthracene (3.617), and the A-ring of pyrene (3.574). This order is in accord with the order of decreasing localization energies, previously reported by Nicholson.[4] The published results indicate that chromium hexacarbonyl reacts with the terminal A-rings of each of these PAHs,[3,4,21] which have the highest total π-bond order in each of the PAH molecules. It has been found that the tricarbonylchromium complexes with benzene, biphenyl, and phenanthrene are more stable than those with pyrene or anthracene.[4,21] These findings are in accord with the prediction based on the total π-bond order of the benzenoid ring coordinated to chromium. Benzo[*b*]fluorene and fluoranthene are the two structural isomers that contain a benzene ring and a naphthalene ring. It has also been found that reaction of chromium hexacarbonyl with benzo[*b*]fluorene and fluoranthene occurred at the benzenoid moiety, rather than at the naphthalenoid moiety.[20] These results again support the premise that the total π-bond order of a benzenoid ring in a PAH is the decisive factor in determining the regioselective preference of the coordination reactions.

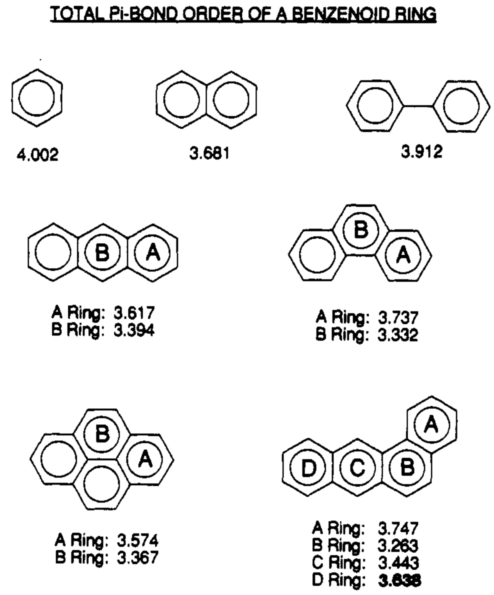


Figure 3. Calculated total π-bond orders of the benzenoid rings of benzene, naphthalene, biphenyl, anthracene, phenanthrene, pyrene, and benz[*a*]anthracene. The single π-bond orders of these molecules are calculated by the simple LCAO–MO method, obtained from ref 35.

It is also worth noting that coordination of benz[*a*]anthracene at the A-ring (Figure 3) retains the anthracene structural unit, while coordination at the D-ring, the benzo ring of benz[*a*]anthracene with the second highest total π-bond order, retains the phenanthrene structural unit. However, the difference between the empirical resonance energies of benz[*a*]anthracene and phenanthrene is 28.1 kcal, while the difference between benz[*a*]anthracene and anthracene is 20.3 kcal.[37] Thus, coordination of benz[*a*]anthracene at the D-ring should be approximately 7.8 kcal more favored than coordination at the A-ring. This discrepancy suggests that coordination reaction between PAHs and chromium hexacarbonyl, to form (η^6-arene)tricarbonylchromium complexes, is not determined by the stability of the resulting products. However, it supports our hypothesis that regioselectivity is controlled by the total π-bond order (or the total π-electron density) of the benzenoid ring in a PAH.

We report in this paper that the reactions of 9-methylanthracene (**2a**) and 9,10-dimethylanthracene (**3a**) occur regioselectively at the central aromatic ring. This is in contrast with previous reports that the $Cr(CO)_3$ moiety is always attached to a terminal rather than to a central aromatic ring.[4] These results suggest that the inductive effect of the methyl substituent can enhance the total

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(35) Streitwieser, A., Jr.; *Molecular Orbital Theory for Organic Chemists*; John Wiley & Sons, Inc.: New York, 1961.

(36) Higasi, K.; Baba, H.; Rembaum, A. *Quantum Organic Chemistry*; Interscience Publishers: New York, 1965.

(37) Reference 35, p 241.

π-electron density at the central ring and thereby be sufficient to direct the [Cr(CO)$_3$] group to the central ring. However, the effect of a methyl group attached to the benz[*a*]anthracene molecule on the regioselectivity of the reaction is much less than that of the methyl-substituted anthracene. These results suggest that the terminal benzo-ring (A) of benz[*a*]anthracene is strongly favored for coordination with chromium.

Because of the strong electron-withdrawing character of the chromium tricarbonyl moiety, (η^6-arene)tricarbonylchromium complexes have been utilized to synthesize compounds that cannot be obtained by convenient organic reactions.[3,5–19] In particular, a variety of nucleophilic aromatic substitution reactions can be carried out on the aromatic system as well as stereospecific reactions on the functional groups which are attached to the aromatic ring. However, most of the reactions involve only the (η^6-arene)tricarbonylchromium complexes that are derived from benzene, naphthalene, and their substituted derivatives. Little is known about how these complexes can be utilized for reactions at the neighboring aromatic moiety and the functional groups of these complexes. With the complexes available from our syntheses, study of such reactions is now possible.

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