(25 mg, 0.057 mmol).[29] Following evacuation of the apparatus, ca. 0.6 mL of THF-d_8 was vacuum distilled into it and the tube was flame-sealed. The tube was shaken vigorously while being allowed to warm to ambient temperature. The [(Me$_3$P)$_4$Rh]$^+$Cl$^-$, which is normally insoluble in THF at room temperature, quickly dissolved to afford a homogeneous red solution. Examination of the ^{31}P{^{1}H} NMR spectra recorded at daily intervals revealed the disappearance of the two reactants with the appearance of signals attributable to (*o*-MeC$_6$H$_4$)Rh(PMe$_3$)$_3$[25] and (*o*-MeC$_6$H$_4$)Rh-(PMe$_3$)(dtbpe).[13]

Reaction of (dtbpe)Rh(C$_6$H$_5$)$_2$Li(OEt$_2$)$_{1.6}$ with ClIr-(PMe$_3$)(dtbpe). The NMR tube apparatus described above was charged with (dtbpe)Rh(C$_6$H$_5$)$_2$Li(OEt$_2$)$_{1.6}$ (40 mg, 0.057 mmol) and ClIr(PMe$_3$)(dtbpe) (35 mg, 0.057 mmol). The apparatus was evacuated, and then ca. 0.6 mL of THF-d_8 was vacuum distilled into the tube. After the NMR tube was flame-sealed, it was shaken vigorously while being allowed to warm to room temperature. The color of the solution gradually changed from yellow to red. Examination of the ^{31}P{^{1}H} NMR spectrum revealed that (C$_6$H$_5$)-Ir(PMe$_3$)(dtbpe)[13] had been formed. Several other unidentified phosphorus-containing products were also present.

Reaction of (dippe)Rh(*p*-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ with *p*-MeC$_6$H$_4$Li. An NMR tube was charged with 50 mg (0.074 mmol) of (dippe)Rh(*p*-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ and 20 mg (0.127 mmol) of *p*-MeC$_6$H$_4$Li·0.8OEt$_2$. After the tube was evacuated and ca. 0.5 mL of THF-d_8 was vacuum distilled into, it was flame sealed. The ^{13}C{^{1}H} NMR spectrum of this sample showed distinct environments for "free" and "rhodium-bound" *p*-tolyllithium, although the resonances were broadened. Coupling information was generally erased except for the aryl ipso resonance which, although

very broad, still displayed coupling to the phosphorus trans to it.

Registry No. 1, 107820-53-1; 2, 107820-59-7; 3, 107820-57-5; [(dtbpe)Rh(C$_6$H$_5$)$_2$]li, 107846-40-2; [(dtbpe)Rh(*p*-MeC$_6$H$_4$)$_2$]Li, 107820-51-9; [(dtbpe)Rh(*o*-MeC$_6$H$_4$)$_2$]Li, 107820-52-0; [(dtbpe)-Rh(*p*-MeC$_6$H$_4$)$_2$]Li(tMeda), 107820-56-4; [(dippe)Rh(*p*-MeC$_6$H$_4$)$_2$]Li, 107820-56-4; [(dtbpe)IrMe$_2$]Ki, 107820-58-6; [(dtbpe)Ir(C$_6$H$_5$)$_2$]Li, 107820-60-0; [(dtbpe)Ir(*p*-MeC$_6$H$_4$)$_2$Li, 107820-61-1; [(dtbpe)Ir(CCCMe$_3$)$_2$]Li, 107820-62-2; [(μ-D)Rh-(dtbpe)]$_2$, 107820-63-3; [(μ-H)Rh(dtbpe)]$_2$, 107820-64-4; [(μ-OH)IR(dtbpe)]$_2$, 107820-64-4; [(μOH)Ir(dtbpe)]$_2$, 107820-65-5; [(Me$_3$P)4Rh]Cl, 70525-09-6; (*o*-Me(C$_6$H$_4$)Rh(PMe$_3$)$_3$, 77682-07-6; (*o*-Me(C$_6$H$_4$)Rh(PMe$_3$)(dtbpe), 107820-66-6; ClIr(PMe$_3$)(dtbpe), 107820-67-7; (C$_6$H$_5$)Ir(PMe$_3$)(dtbpe), 107820-68-8; (dtbpe)Ph-(CCCMe$_3$(2, 107846-41-3; [(dtbpe)RhMe$_2$]Li, 107820-69-9; [(dtbpe)Rh(CH$_2$SiMe$_3$)$_2$]Li, 107820-70-2; PhLi, 591-51-5; *p*-CH$_3$C$_6$H$_4$Li, 2417-95-0; *o*-CH$_3$C$_6$H$_4$Li, 6699-93-0; Me$_3$CCCLi, 37892-71-0; Me$_3$SiCH$_2$Li, 1822-00-0; *tert*-butylacetylene, 917-92-0.

Supplementary Material Available: Complete tabulations of ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopic data obtained for the complexes (dtbpe)MR$_2$Li(OR'$_2$)$_x$ (M = Rh, Ir), (dtbpe)Rh-(*p*-MeC$_6$H$_4$)$_2$Li(tmeda), and (dippe)Rh(*p*-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ as well as comparisons of carbon NMR parameters between (dtbpe)MR$_2$Li(OR'$_2$)$_x$ and RM(PMe$_3$)(dtbpe) (Tables II–V, respectively) (14 pages). Ordering information is available on any current masthead page.

(29) Werner, H.; Fesser, R.; Buchner, W. *Chem. Ber.* 1979, *112*, 834.

Transition-Metal Organometallic Compounds. 8. Arene Exchange Reactions of Bis(naphthalene)chromium

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The synthesis and characterization of (η^6-arene)(η^6-naphthalene)chromium and (μ,η^6,η^6-naphthalene)-bis(η^6-benzene)dichromium compounds formed in the ligand exchange reaction of bis(η^6-naphthalene)-chromium with fluorobenzene, benzene, toluene, mesitylene, and hexamethylbenzene in THF are described. The reaction also produces hydrogenated products, namely, bis(η^6-tetralin)chromium and (η^6-tetra-lin)(η^6-naphthalene)chromium; these compounds also were independently synthesized and characterized. The ^{1}H NMR spectra and high-resolution mass spectra used in characterizing the compounds are reported. The X-ray crystal structure of the slipped triple-decker (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium is reported. Although the simple arenes produce only the monoexchange products and the corresponding slipped triple-decker products, dimethyldiphenylsilane yielded the double exchange product bis(η^6-di-methyldiphenylsilane)chromium.

Introduction

Since Timms[1] first reported the direct synthesis of bis(arene)chromium π-complexes from metal atoms and the arene, the process has been used to synthesize a rich profusion of compounds incorporating metal–ligand interactions. We are interested here in the chromium complexes of polycyclic arenes like naphthalene (I) which exhibits distinctly different properties than the conventional arene complexes (II): viz., I undergoes ligand exchange under conditions where II does not.[2] Bis(η^6-

I   II
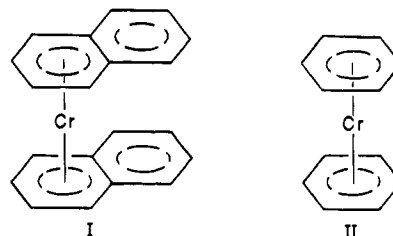
naphthalene)chromium can be made through the direct synthetic route either with the conventional co-condensation technique[3,4] or from the evaporation of metal atoms

(1) Timms, P. L. *J. Chem. Soc. D* 1969, 1033.
(2) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* 1980, 991.

(3) Elschenbroich, C.; Möckel, R. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 870.

into a solution containing the ligand[2] or into the neat ligand.[5,6] At least one of the ligands in bis(η^6-naphthalene)chromium can be exchanged under relatively mild conditions.[2,6] We became interested in the use of this exchange process as a method of producing mixed-arene metal complexes (eq 1). A recent publication[6] describing

$$Cr(C_{10}H_8)_2 + arene \rightarrow Cr(C_{10}H_8)(arene) + C_{10}H_8 \quad (1)$$

the process in eq 1 has prompted us to submit our detailed observations on this system, which are somewhat different than those reported. In our hands the exchange process also produces the binuclear metal species incorporating a μ-bonded naphthalene, (μ,η^6,η^6-naphthalene)bis(η^6-arene)dichromium (eq 2). This new class of compounds

$$2Cr(C_{10}H_8)_2 + 2(arene) \rightarrow$$
$$[(arene)Cr]_2(C_{10}H_8) + 3C_{10}H_8 \quad (2)$$
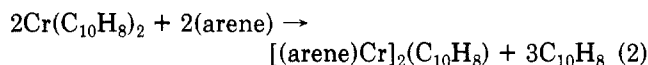
provides the opportunity to study the electronic communication between chromium atoms in the dinuclear species, which is the topic of a forthcoming publication.

In studying these compounds it was our initial intention to devise a synthetic system to provide mixed-arene compounds from bis(η^6-naphthalene)chromium, much like chromium hexacarbonyl can be used to make (arene)-chromium tricarbonyl derivatives. The proposed substituent would have different electron-withdrawing effects than the carbon monoxide[7] which is of interest to our other studies. Bis(η^6-naphthalene)chromium provides an unexpectedly rich chemistry by providing a synthetic route to many novel products. Here we describe exchange processes of bis(η^6-naphthalene)chromium that form (μ,η^6,η^6-naphthalene)bis(η^6-arene)dichromium, (η^6-arene)(η^6-naphthalene)chromium, and bis(η^6-arene)chromium.

Experimental Section

Reagents. Liquid reagents (other than fluorobenzene) were dried over NaK with vigorous stirring. If the reagent contained a substantial amount of water as indicated by the formation of hydroxides, it was vacuum distilled and redried over NaK with vigorous stirring. Sodium benzophenone ketal was not generally used to dry THF for these experiments because we found that benzophenone and its byproducts markedly contaminate the product THF upon distillation. Fluorobenzene was dried by long-term stirring with P_2O_5 and isolated by vacuum distillation.[8] Hexamethylbenzene was sublimed to an ice-cooled cold finger under vacuum.

Synthesis. Bis(η^6-naphthalene)chromium. Although there are a number of referenced synthesis of this compound,[2-5] the following general procedure was developed for use in our work. Onto the liquid-nitrogen-cooled walls of a glass reaction vessel, 1,2-dimethoxyethane, naphthalene, and chromium atoms were co-condensed under high vacuum (less than 10^{-6} torr when ligand and solvent are not present in the system). The rate of co-condensation into a 3.8-L reaction vessel generally were, approximately, 5 mL/h for 1,2-dimethoxyethane, 5 g/h for naphthalene, and 0.5 g/h for chromium. The naphthalene was sublimed from an internal effusion cell that was equipped with a heat shield to regulate radiant heat. The 1,2-dimethoxyethane can be omitted from the condensation if desired. After all reagents had been

evaporated, the reaction matrix was allowed to warm to room temperature. The reaction product and excess naphthalene are removed from the reaction vessel through a cannula by using 1,2-dimethoxyethane as a solvent. The solution was passed through a fritted filter, the solvent removed by vacuum distillation, and excess naphthalene removed from the resulting solid by sublimation. Continued sublimation provided bis(η^6-naphthalene)chromium. Typical yields of bis(η^6-naphthalene)-chromium for a 4-h reaction are 0.7–0.8 g or 6–7% on the basis of chromium vaporized (approximately 2 g). The product of this procedure exhibited the ^1H NMR[2,9] and mass[3] spectra reported previously.

Exchange Reactions. All exchange reactions were conducted in sealed glass ampules at elevated temperatures in the presence of rigorously dried THF. In a typical reaction, bis(η^6-naphthalene)chromium (150 mg, 0.487 mmol), benzene (5.0 mL, 56.1 mmol), and THF (1.5 mL 18.5 mmol) were sealed in a glass ampule and heated in a boiling water bath for 45 min with occasional agitation. The resulting homogeneous reaction mixture was dark brown; a dark solid precipitated when the mixture cooled. The ampule was opened by using standard Schlenk techniques, and the contents were transferred to a Schlenk flask by using a metal cannula: excess dry THF was used to effect quantitative transfer. The solvent and unreacted benzene were removed by vacuum distillation; the displaced naphthalene in the remaining mixture was removed by vacuum sublimation. The resulting mixture was then heated to 60 °C to remove hydrogenated products by sublimation (to a liquid-nitrogen-cooled cold finger). When continued sublimation under these conditions apparently stopped producing the byproducts, the residue was redissolved in dry THF, the solvent was removed under vacuum, and the residue was again subjected to sublimation under the same conditions. This entire process was repeated a third time, after which sublimation byproducts ceased to be produced. The final residue was then heated carefully with a heat gun and sublimed to a clean liquid-nitrogen-cooled cold finger yielding 60 mg of product, 57% based on bis(η^6-naphthalene)chromium used. HRMS for (η^6-benzene)(η^6-naphthalene)chromium: calcd for $C_{16}H_{14}Cr$ 258.050 06, found 258.049 54, error (mamu/ppm) –0.52/2.0. HRMS for (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium: calculated for $C_{22}H_{20}Cr_2$ 388.037 514, found 388.037 848, error (mamu/ppm) 0.33/0.86.

The NMR assay of this product showed it to be 42% (η^6-benzene)(η^6-naphthalene)chromium and 58% (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (vide infra).

A summary of the details of reactions of this and other arenes with bis(η^6-naphthalene)chromium appears in Table I.

An exchange reaction reproducing the conditions described in ref 6 was performed. A mixture of bis(η^6-naphthalene)chromium (220 mg, 0.714 mmol), benzene (5 mL, 56.1 mmol), and THF (0.2 mL, 2.5 mmol) was sealed in a glass ampule and heated at 97 °C for 23 h in an oil bath. The reaction mixture was removed to a Schlenk flask by using a mixture of hexanes to effect quantitative transfer. The solvent and unreacted ligand were removed by vacuum distillation, and naphthalene was sublimed to a liquid-nitrogen-cooled cold finger. The remaining organometallic product was dissolved in a mixture of hexanes and filtered through dry deoxygenated Celite. The hexane solvent was then removed by distillation until approximately 15 mL remained, and the flask placed in dry ice overnight. The hexanes were then removed via cannula filter, and the solid residue was dried under vacuum; yield 70 mg, 46% based on bis(η^6-naphthalene)chromium. NMR assay: (η^6-benzene)(η^6-naphthalene)chromium, 75%; (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium, 3%; (η^6-tetralin)(η^6-naphthalene)chromium, 22%.

Bis(η^6-tetralin)chromium: Chromium (1.806 g, 24.7 mmol) was evaporated onto the walls of a liquid-nitrogen-cooled vessel while approximately 35 mL (257 mmol) of tetralin was distilled into the vessel over a period of 5 h. The reaction product was dissolved in 1,2-dimethoxyethane, removed from the reaction vessel with a cannula, and filtered through a glass frit to remove unreacted chromium metal. The solvent and excess tetralin were removed by vacuum distillation. The residue was sublimed to

(4) Bard, R. A.; Lagowski, J. J. Presented at the 175th National of the American Chemical Society, Meeting Anaheim, CA March 1978; *Bis-(naphthalene)chromium: Preparation and Properties*.

(5) The synthesis of bis(η^6-naphthalene)chromium has been accomplished by the method described by: Markle, R. J.; Pettijohn, T. M.; Lagowski, J. J. *Organometallics* **1985**, *4*, 1529.

(6) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286* 1983.

(7) Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Rudonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938.

(8) Perrin, D. D.; Armarego, W. F. L.; Perrin, D. R. *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon: New York, 1980.

(9) Elschenbroich, C.; Möckel, R.; Massa, W.; Birkhahn, M.; Zenneck, U. *Chem. Ber.* **1982**, *115*, 334.

Table I. A Summary of the Reactions of Arenes with Bis(η^6-naphthalene)chromium

arene	amt of Cr(C$_{10}$H$_8$)$_2$,[d] mg	arene/THF	t,[e] h	n[f]	yield, %	NMR assay double decker triple decker	high-resolutn mass spectroscopy calcd	found	error (in mamu/ppm)	other
fluorobenzene	150	5 mL/1.5 mL	2.0	3	5	18% 76%	276.04064 424.0187	276.04006 424.0201	-0.57/2.1 1.4/3.2	6% Cr$_2$(C$_{10}$H$_8$)(C$_6$H$_6$)$_2$[g]
benzene	150	5 mL/1.5 mL	0.75	3	57	42% 58%	258.05006 388.037514	258.04954 388.037848	-0.52/2.0 0.33/0.86	
benzene[a]	220	5 mL/0.2 mL	23	none[b]	46	75% 3%	k k			22% Cr(C$_{10}$H$_{12}$)(C$_{10}$H$_8$)[h]
toluene	150	5 mL/1.5 mL	2.5	3	27	35% 65%	272.06570 416.0688	272.06520 416.0672	-0.51/1.9 -1.6/4.0	
mesitylene	150	5 mL/1.5 mL	2.0	3	20	24% 59%	300.09700 472.1314	300.09666 472.1326	-0.35/1.2 1.2/2.6	17% Cr(C$_{10}$H$_8$)$_2$[d]
hexamethylbenzene	150	1.5 g/7 mL	1.0	3	18	88% 0%	342.14395 l	342.14450 l	0.55/1.6	12% Cr(C$_{10}$H$_8$)$_2$[d]
tetralin	150	5 mL/1.5 mL	2.0	none	56	100% 0%	312.0970 l	312.0956 l	-1.4/4.6	
dimethyldiphenylsilane	200	5 mL/0.5 mL	1.0	3	16	k	392.10523 476.144756	392.10362 476.14576	-1.6/4.1 1.2/2.5	Cr[Si(CH$_3$)$_2$(C$_6$H$_5$)$_2$](C$_{10}$H$_8$)[i] Cr[Si(CH$_3$)$_2$(C$_6$H$_5$)$_2$]$_2$[j]

a Synthesis performed according to ref 6. *b* See text for procedures. *c* Double decker = (η^6-arene)(η^6-naphthalene)(η^6-naphthalene)chromium. Triple decker = (μ,η^6,η^6-naphthalene)bis(η^6-arene)dichromium. *d* Cr(C$_{10}$H$_8$)$_2$ = bis(η^6-naphthalene)chromium. *e* Reaction times at 100 °C. *f* Number of purification sublimations. *g* Cr$_2$(C$_{10}$H$_8$)(C$_6$H$_6$)$_2$ = (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium-like species. *h* Cr(C$_{10}$H$_{12}$)(C$_{10}$H$_8$) = (η^6-tetralin)(η^6-naphthalene)chromium. *i* Cr[Si(CH$_3$)$_2$-(C$_6$H$_5$)$_2$](C$_{10}$H$_8$) = (dimethyldiphenylsilane)(naphthalene)chromium. *j* Cr[Si(CH$_3$)$_2$(C$_6$H$_5$)$_2$]$_2$ = bis(dimethylphenylsilane)chromium. *k* Not performed. *l* Performed; not found.

a liquid-nitrogen-cooled cold finger by careful heating with a heat gun; yield 2.00 g, 18% (based on chromium). HRMS: calcd for C$_{20}$H$_{24}$Cr 316.128301, found 316.128649, error (mamu/ppm) 0.35/1.10.

Spectroscopy. Proton NMR spectra were recorded with a 200-MHz (Nicolet Instruments Corp. NT200) or a 500-MHz (General Electric GN500) spectrometer. The preparation of the samples required the rigorous exclusion of water and oxygen, which was accomplished by drying the NMR solvents (benzene d_6, toluene d_8, or THF d_8 over NaK with vigorous stirring. The dry solvents were then degassed in three freeze–(liquid nitrogen)–degas–thaw cycles. The dry and oxygen-free solvent prepared by this procedure was stored in sealed ampules in quantities sufficient to prepare one NMR sample per ampule. The NMR tubes were sealed with a flame. At no time was either the solvent or the sample allowed to come in contact with the air. The spectra are referenced to the solvent (C$_6$D$_6$, 7.15 ppm) and are reported in parts per million in Tables II–IV. Table II contains the chemical shifts and splittings of the (η^6-arene)(η^6-naphthalene)chromium isomers, while Table III incorporates the spectra of the slipped triple-decker compounds. Table IV contains the spectra of compounds synthesized to assay the reaction mixtures and bis(η^6-naphthalene)chromium; the absence of these compounds in the mixture is taken as a measure of its purity.

Low-resolution mass spectra were obtained on a Bell & Howell Model 21-491 spectrometer incorporating an INCOS data system using 70-eV electron-impact ionization; the parent ion complete with the appropriate chromium isotope pattern was generally observed. Fragments typically observed were (arene)(naphthalene)chromium, arene–chromium, and naphthalene–chromium species, as well as the free ligands.

Elemental analysis were established from high-resolution mass spectra obtained on a Consolidated Electrodynamics Corp. Model 21-110B spectrometer with 70-eV electron-impact ionization.

The thermal sensitivity of the compounds of interest[3] required that a special technique be developed that would allow them to be sublimed with minimal decomposition into the spectrometer. This technique maximizes the surface area of the sample in order to more readily sublime it. All operations were carried out in a helium filled drybox, the atmosphere of which was in equilibrium with NaK liquid alloy. A small quantity of product is placed in a common melting point capillary. NaK-dried THF is then injected into the capillary with a 100-μL syringe while the needle was slowly withdrawn from the capillary. The THF is then shaken down into the bottom of the capillary and the capillary inverted to dissolve the compound. The capillary is then placed in the drybox airlock and the pressure decreased gradually over $^1/_2$ h to evaporate the THF without bumping. The airlock is then refilled with helium and the capillary brought back into the drybox to be sealed with a plug of silicone grease so that it can be flame sealed after removal from the drybox.

In a special experiment intended to establish the optimal conditions required for successful mass spectrometry of these compounds, two identical samples of a mixture of (η^6-benzene)(η^6-naphthalene)chromium and (μ,η^6,η^6-naphthalene)-bis(η^6-benzene)dichromium prepared as described above were analyzed mass spectroscopically with a Finnigan MAT 4023 mass spectrometer with an INCOS data system. One sample was analyzed with 70-eV electron-impact ionization, while the other was subjected to chemical ionization by using 70-eV ionized methane. The mass intensity of the species of interest was plotted throughout the two runs. The data indicated that free naphthalene appeared well before the organometallic compound began to be detected with both electron-impact and chemical ionization processes. The detection of free naphthalene from a sample known not to contain free naphthalene (by NMR analysis) clearly indicated the thermal decomposition of the organometallic species. As expected the chemical ionization technique resulted in an enhanced intensity due to (η^6-benzene)(η^6-naphthalene)chromium, but surprisingly the intensity due to (μ,η^6,η^6-naphthalene)bis-(η^6-benzene)dichromium was not improved.

X-ray Data for (μ,η^6,η^6-Naphthalene)bis(η^6-benzene)dichromium. A thin, dark red crystal, 0.02 mm × 0.28 mm × 0.38 mm, formed by slow cooling of a hot benzene–THF solution (1.75:1.25 v/v), was sealed in a thin walled capillary in a helium atmosphere. Data were collected on a Syntex P2$_1$ diffractometer,

Table II. NMR Chemical Shifts (δ) for (η^6-Arene)(η^6-naphthalene)chromium Compounds[a]

ligand	η^6-arene substituent resonances				η^6-naphthalene resonances[e]			
	methyl	ortho	meta	para	a	b	c	d
fluorobenzene[b]		4.47 d	3.79 t	3.65 q	4.35 m	5.57 m	6.90 m	7.45 m
A		4.95	5.28	5.32	14.05	12.72	13.52	12.72
B						610.97	279.52	
benzene[b]			(4.03 s)		4.35 m	5.51 m	6.90 m	7.56 m
A					8.67	8.94	14.19	14.45
B						577.53	292.10	
toluene[b]	1.72 s	3.94	4.15 t	4.06 t	4.31 m	5.39 m	6.94 m	7.52 m
A		d	5.40	5.72	9.72	9.72	14.19	14.45
B						540.07	292.10	
mesitylene[c]	1.89 s		(3.96 s)		4.17 m	5.17 m	6.98 m	7.51 m
A					7.47	8.41	11.57	12.30
B						199.94	107.17	
hexamethylbenzene[c]	1.94 s				3.92 m	4.79 m	7.04 m	7.43 m
A					6.94	7.57	10.83	11.36
B						173.40	82.60	

[a] A, peak width at half peak height, Hz; B, coupling between corresponding peaks measured center to center, Hz. [b] Data from 500-MHz spectrometer. [c] Data from 200-MHz spectrometer. [d] Resonance obscured, observed by integration; resonance is predicted to be doublet. [e] Proton positions on complexed naphthalene moiety defined by
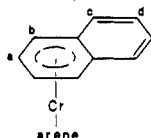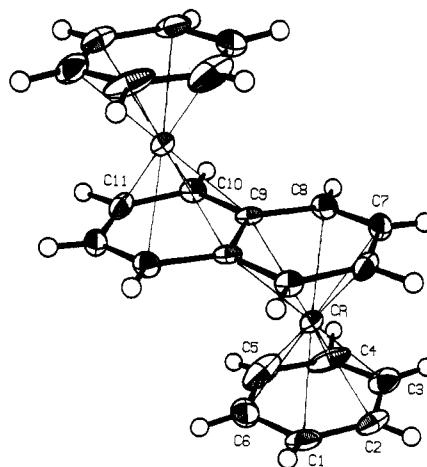
Table III. NMR Chemical Shifts in (δ) for (μ,η^6,η^6-Naphthalene)(bis(η^6-arene)dichromium Compounds

ligand[a]	η^6-arene substituent resonances				μ,η^6,η^6-naphthalene resonances[d]	
	methyl	ortho	meta	para	a	b
$C_6H_5F^b$		4.25 d	3.50 t	3.75 q	4.01 m	5.49 m
A		5.07	4.91	5.30	2.03	2.02
B					738.43	
$C_6H_6^b$			(3.89 s)		3.97 m	5.67 m
A					8.41	8.94
B					847.74	
$C_6H_5CH_3^c$	1.67 s	3.85 d	3.98 t	3.91 t	3.94 m	5.49 m
A		5.14	5.24	5.05	9.72	9.72
B					773.75	
C_6H_3-$(CH_3)_3^c$	1.83 s		(3.87 s)		3.23 m	3.77 m
A					9.15	8.20
B					293.51	

[a] A, peak width measured at half peak height, Hz; B, coupling between resonances measured center to center, Hz. C_6H_5F = fluorobenzene; C_6H_6 = benzene; $C_6H_5CH_3$ = toluene; $C_6H_3(CH_3)_3$ = mesitylene. [b] Data from 500 MHz spectrometer. [c] Data from 200-MHz spectrometer. [d] Proton position on complexed naphthalene moiety as defined by

Figure 1. ORTEP and atom numbering scheme for (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (IX). H atoms are of an arbitrary radius.

with a graphite monochromator, using Mo Kα radiation (λ = 0.710 69 Å) and equipped with a Syntex LT-1 low-temperature (163 K) delivery system. Lattice parameters were obtained from least-squares refinement of 44 reflections with $18.8° < 2\theta < 27.1°$, a = 9.251 (7) Å, b = 7.921 (4) Å, c = 10.927 (8) Å, β = 100.12 (4)°, V = 788.2 (9) Å^3, ρ_{calcd} = 1.64 g/cm^3. The crystal system is monoclinic, the space group is $P2_1/n$, and Z = 2. The compound lies on a center of symmetry that is located halfway between the bridgehead carbon atoms of the naphthalene moiety. Data were collected by using the ω scan technique (3687 reflections, 1806 unique, R_{int} = 0.0311), over a 2θ range from 4.0 to 55.0°, with a 1° ω scan at 2.5–5.0°/min (h = $-2 \rightarrow 10$, k = $-10 \rightarrow 10$, l = $-14 \rightarrow 14$). Four reflections (002, $\bar{2}$00, $\bar{1}$11, 00$\bar{1}$) were remeasured every 96 reflections to monitor instrument and crystal stability. Data were corrected for Lp effects, absorption (based on crystal shape; μ = 13.45 cm^{-1}, transmission factor range 0.6492–0.9577), and decay (maximum correction on I < 2%[10]). Data reduction is

described in Riley and Davis.[11] Reflections having $F_o < 4(\sigma(F_o))$ were considered unobserved (418 reflections). The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures[12] with anisotropic thermal parameters for the non-H atoms. H atom positions were located from a difference electron density map and refined with isotropic thermal parameters. A total of 149 parameters were refined. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/(\sigma(F_o))^2$. Final R = 0.0542 for 1388 reflections, wR = 0.0422 (R_{all} = 0.0780, wR_{all} = 0.0439), and a goodness of fit, S, equals 2.04. Maximum |shift/esd| < 0.1 in the final refinement cycle, and the minimum and maximum peaks in the final ΔF map were −0.56 and 0.68 e/Å^3, respectively. Scattering factors for the non-H atoms were from Cromer and Mann,[13] with anomalous dispersion corrections from Cromer and Liberman,[14] while scattering factors for the H atoms were from Stewart, Davidson, and Simpson;[15] linear absorption coefficient

(10) Henslee, W. H.; Davis, R. E. *Acta Cryst.* **1975**, *B31*, 1511–1519.

(11) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381–386.

(12) Sheldrick, G. M. SHELX76, program for crystal structure determination; University of Cambridge: Cambridge England, 1976.

(13) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321–324.

(14) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Phys. Chem.* **1965**, *42*, 3175–3187.

Table IV. NMR Chemical Shifts (δ) for Contaminants[a]

	e[d]	f[d]	g[d]	h[d]		a[e]	b[e]	c[e]	d[e]
(η^6-tetralin)(η^6-naphthalene)chromium[b]	4.18 m	3.94 m	2.29 m	1.68 m	1.44 m	4.31 m	5.20 m	6.99 m	7.53 m
A	8.10	8.41		28.18	19.14	19.56	8.20	8.41	12.30	12.62
B		47.97			48.79		179.30		106.90	
C				145.91						
bis(η^6-naphthalene)chromium[c]						4.37 m	5.29 m	(6.92 s)	
A						7.47	7.47	2.84	
B						183.06			
bis(η^6-tetralin)chromium[b]	4.18 m	4.04 m	2.73 m	2.43 m	1.77 m	1.50 m			
A	10.09	10.09	22.71	22.71	15.14	15.14			
B		28.08		58.71		53.72			
C				188.95					

[a] A, peak width at half peak height, Hz; B, coupling between peaks measured center to center, Hz; C, coupling between multiplets measured center to center, Hz. [b] Data from 200-MHz spectrometer. [c] Reference 9. [d] Proton position on complexed tetralin moiety. [e] Proton position on complexed naphthalene moiety as defined by
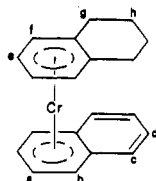
Table V. Fractional Coordinates and Isotropic or Equivalent Isotropic[a] Thermal Parameters (Å^2) for Non-Hydrogen Atoms of $C_{22}H_{20}Cr_2$

atom	x	y	z	U
Cr	0.18137 (8)	0.15625 (9)	−0.00569 (6)	0.0153 (2)
C(1)	0.3225 (6)	0.1614 (7)	−0.1415 (5)	0.031 (2)
C(2)	0.3908 (6)	0.2403 (6)	−0.0368 (5)	0.028 (2)
C(3)	0.3213 (6)	0.3723 (5)	0.0159 (5)	0.030 (2)
C(4)	0.1815 (6)	0.4241 (6)	−0.0408 (6)	0.036 (2)
C(5)	0.1073 (6)	0.3388 (8)	−0.1431 (6)	0.045 (2)
C(6)	0.1778 (6)	0.2048 (7)	−0.1967 (5)	0.039 (2)
C(7)	0.1895 (5)	0.0958 (6)	0.1869 (4)	0.0216 (14)
C(8)	0.0497 (5)	0.1518 (6)	0.1363 (4)	0.0200 (13)
C(9)	−0.0347 (5)	0.0679 (5)	0.0300 (4)	0.0162 (13)
C(10)	−0.1851 (5)	0.1083 (5)	−0.0203 (4)	0.0181 (14)
C(11)	−0.2577 (5)	0.0338 (5)	−0.1293 (4)	0.0207 (13)
H(1)	0.347 (6)	0.070 (6)	−0.171 (4)	0.04 (2)
H(2)	0.474 (6)	0.230 (7)	−0.001 (5)	0.06 (2)
H(3)	0.361 (5)	0.423 (5)	0.087 (4)	0.020 (12)
H(4)	0.122 (6)	0.509 (6)	−0.005 (5)	0.05 (2)
H(5)	0.036 (5)	0.359 (6)	−0.174 (4)	0.023 (14)
H(6)	0.137 (5)	0.158 (6)	−0.269 (4)	0.017 (11)
H(7)	0.241 (5)	0.145 (5)	0.248 (4)	0.032 (13)
H(8)	0.008 (4)	0.237 (5)	0.168 (3)	0.012 (11)
H(10)	−0.223 (5)	0.185 (5)	0.015 (4)	0.017 (12)
H(11)	−0.360 (5)	0.062 (5)	−0.170 (4)	0.031 (13)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct space unit cell vectors.

were from ref 16. The least-squares planes program was supplied by Cordes;[17] other computer programs were from ref 11 of Gadol and Davis.[18]

Discussion

The synthesis and characterization of the arene exchange products of bis(η^6-naphthalene)chromium are unusually difficult because of their extraordinary sensitivity and reactivity. Special handling techniques had to be devised to ensure contamination of the products with the atmosphere never occurred, since even slight contamination ultimately leads to autocatalytic decomposition and loss of the entire sample. Characterization of the compounds is difficult because of the equivocal nature of most characterization techniques when applied to the com-
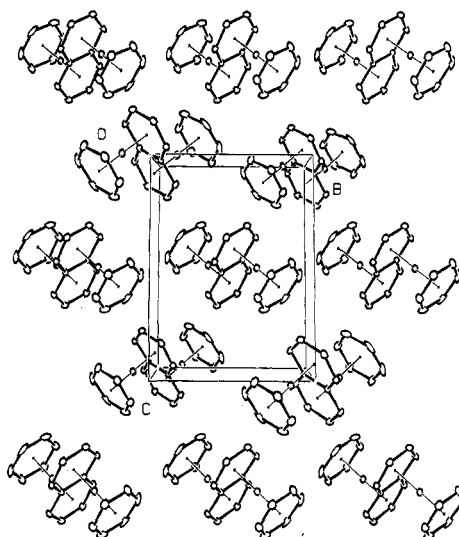
Figure 2. Packing diagram of (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (IX).

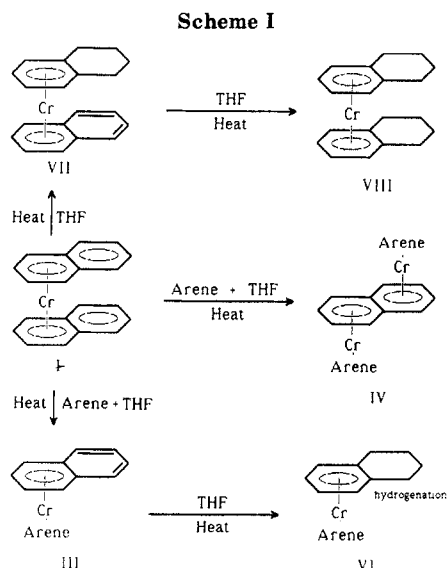**Table VI. Bond Lengths (Å) and Angles (deg) for Cr and the Phenyl Ring (Non-H) in $C_{22}H_{20}Cr_2$[a]**

1	2	3	1-2	1-2-3
Cr	C(1)		2.142 (6)	
Cr	C(2)		2.132 (6)	
Cr	C(3)		2.134 (5)	
Cr	C(4)		2.156 (5)	
Cr	C(5)		2.110 (6)	
Cr	C(6)		2.117 (5)	
Cr	C(7)		2.147 (5)	
Cr	C(8)		2.134 (5)	
Cr	C(9)		2.216 (5)	
Cr	C(9)*		2.222 (4)	
Cr	C(10)*		2.114 (4)	
Cr	C(11)*		2.139 ((4)	
NC	Cr	BC	1.630 (2)	178.8 (1)
BC	Cr		1.612 (2)	
C(2)	C(1)	C(6)	1.358 (7)	120.9 (5)
C(6)	C(1)		1.411 (7)	
C(3)	C(2)	C(1)	1.404 (7)	120.6 (5)
C(4)	C(3)	C(2)	1.394 (7)	119.5 (5)
C(5)	C(4)	C(3)	1.381 (8)	120.5 (5)
C(6)	C(5)	C(4)	1.425 (9)	119.9 (5)
C(1)	C(6)	C(5)		118.3 (5)

[a] Atoms labeled with an asterisk are related by −x, −y, −z. BC and NC are the centers of the mass of benzene (BC) and one ring in naphthalene (NC).

(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, p 55.

(17) Cordes, A. W., personal communication, 1983.

(18) Gadol, S. M.; Davis, R. E. *Organometallics* 1982, 1, 1607–1613.

Scheme I

VII

THF
Heat

VIII

Heat | THF

I

Arene + THF
Heat

Arene
Cr
Cr
Arene
IV

Heat | Arene + THF

III
Cr
Arene

THF
Heat

Cr
Arene
hydrogenation
VI

pounds obtained. The mass spectra do not typically show the parent ion of the $(\mu,\eta^6,\eta^6$-naphthalene)bis(η^6-arene)-dichromium compounds even while special techniques capture the $(\eta^6$-arene)(η^6-naphthalene)chromium parent ion clearly. The NMR spectra were likewise difficult to interpret, integration being somewhat equivocal. Experiments were conducted to eliminate the possibility that stereochemically nonrigid behavior[19] was the cause of the observed NMR spectra, haptotropic shifts being of special interest.[20,21] The X-ray crystal structure of $(\mu,\eta^6,\eta^6$-naphthalene)bis(η^6-benzene)dichromium makes our assignment definitive.

The exchange process to produce mixed arene–chromium compounds (III and IV, Scheme I) also produces hydrogenation products.[22] An independent experiment shows that bis(η^6-naphthalene)chromium undergoes hydrogenation in THF solution (in the absence of an arene) to produce partially saturated, but still complexed, derivatives of naphthalene(VII); the end product of this process is bis(η^6-tetralin)chromium (VIII). This is an important observation in our understanding of the exchange reaction because η^6-complexed arenes are not known to undergo exchange with free arenes except in the presence of a catalyst.[6] Thus, the hydrogenation of the naphthalene moiety by THF is a competing reaction that removes exchangeable groups from the chromium atom which decreases the yield of the desired mixed arenes (III and IV). The appearance of hydrogenated mixed-ligand products (VI) in the reaction mixture suggests that the naphthalene unit attached to a (arene)chromium moiety can also undergo hydrogenation. The validity of this suggestion was verified by a direct experiment. Thus, a sample (10 mg) of (η^6-benzene)(η^6-naphthalene)chromium dissolved in 2 mL of THF and heated to 80–85 °C for 48 h in a glass ampule undergoes hydrogenation to the extent that approximately half the chromium containing organometallic species consist of hydrogenated (η^6-benzene)(η^6-naphthalene)chromium, as judged from mass spectroscopy. Interestingly the hydrogenation process does not proceed to completion. The naphthalene moiety gains two hydrogen atoms as indicated by the 260 mass peak [benz-

ene(naphthalene + 2 H)chromium] and the 182 mass peak [(naphthalene + 2 H)chromium fragment] and only very small amounts of (η^6-benzene)(η^6-tetralin)chromium (mol wt 262) are formed. As is usually the case in processes involving bis(η^6-naphthalene)chromium, a small amount of chromium metal was also produced.

The hydrogenated species are separated with difficulty from the desired product. The hydrogenated impurities complicate the NMR spectra, especially in view of the relatively low solubility of the target compounds in C_6D_6. The presence of hydrogenated naphthalene-containing products can be easily detected as broad resonances in the NMR spectrum at 2.3, 1.7, and 1.4 ppm, which correspond to the saturated protons of (η^6-tetralin)(η^6-naphthalene)-chromium. The hydrogenation of the (η^6-arene)(η^6-naphthalene)chromium exchange product I appears to be more difficult than that of bis(η^6-naphthalene)chromium. Thus, the general strategy of our investigation involved isolation of exchange products free of hydrogenation products. The latter, being somewhat more volatile than the (η^6-arene)(η^6-naphthalene)chromium and $(\mu,\eta^6,\eta^6$-naphthalene)bis(η^6-arene)dichromium compounds, could be removed from the reaction from the mixtures by careful sublimation. To avoid entrapment of volatile hydrogenation products within the mass of the nonvolatile products, the reaction mixture was dissolved in THF, the THF removed under vacuum, and the product sublimed; this process was repeated three times to yield a product that was virtually free of hydrogenation products as determined by mass spectrometry and NMR spectroscopy.

Since bis(η^6-naphthalene)chromium is itself relatively involatile, it is necessary that the exchange reaction proceed to completion to avoid bis(η^6-naphthalene)chromium contamination in the product. While the hydrogenation of bis(η^6-naphthalene)chromium is relatively rapid, the (η^6-arene)(η^6-naphthalene)chromium compounds also undergo hydrogenation, and it is important not to allow the reaction to proceed too far beyond the point where bis-(η^6-naphthalene)chromium has been consumed. A 2-h reaction time appears to be optimal for all of the arenes we studied, except benzene. Benzene appears to exchange more rapidly than the other arenes.

Products free from known hydrogenated products exhibit a proton NMR spectrum containing resonances that were not expected for the (η^6-arene)(η^6-naphthalene)-chromium species. Moreover, mass spectral evidence indicates these products to be relatively pure (approximately 95%), in clear contrast to the NMR spectra. The NMR spectrum of the (η^6-arene)(η^6-naphthalene)chromium product clearly shows the presence of two compounds, one of which is not apparent in the low-resolution mass spectrum.

In the most spectroscopically simple case, that of (η^6-benzene)(η^6-naphthalene)chromium product, the proton NMR spectrum (Figure 3b) shows resonances at 4.03 ppm (complexed benzene singlet) and two aa'bb' multiplets. One of these multiplets exhibits groups of resonances at 4.35 and 5.51 ppm for the chromium bound part of the naphthalene moiety and the other an aa'bb' multiplet corresponding to the part of the naphthalene moiety not bound to chromium showing groups of peaks at 6.90 and 7.56 ppm. That both of these groups of resonances are in fact separate aa'bb' systems was confirmed by a COSY[23] experiment, which shows spin–spin coupling between the groups of peaks as designated above; there is no indication of coupling between the two aa'bb' multiplets. The "extra

(19) Jackman, L. M.; Cotton, F. A. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic: New York, 1975; p 377.

(20) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, P. C.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

(21) Kirss, R. U.; Treichel, P. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 853.

(22) Elschenbroich, C.; Möckel, R.; Bilger, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 375.

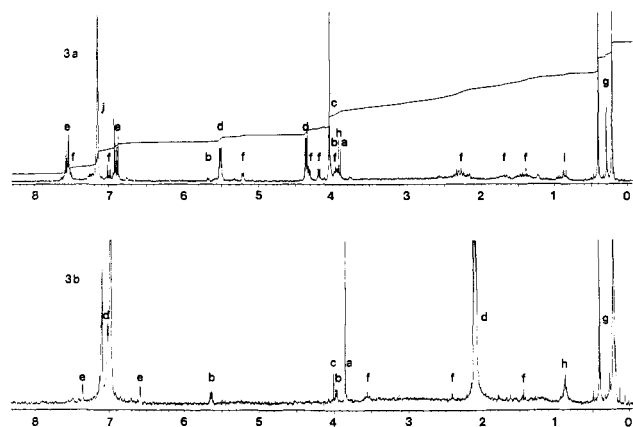(23) Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 371.

Figure 3. Benzene–bis(η^6-naphthalene)chromium exchange mixture, with exchange performed under conditions of ref 6. (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium to (η^6-benzene)(η^6-naphthalene)chromium ratio = 1:25. (μ,η^6,η^6-Naphthalene)bis(benzene)dichromium: (a) benzene, (b) naphthalene, aa'bb'. (η^6-Benzene)(η^6-naphthalene)chromium: (c) benzene, (d) naphthalene, complexed aa'bb', (e) naphthalene, uncomplexed aa'bb', (f) (η^6-tetralin)(η^6-naphthalene)chromium, (g) silicone from grease, (h) unknown impurity, (i) solvent impurity, (j) benzene-d_6. Benzene–bis(naphthalene)chromium exchange mixture. (μ,η^6,η^6-Naphthalene)bis(η^6-benzene)dichromium to (η^6-benzene)(η^6-naphthalene)chromium ratio = 58:42 (μ,η^6,η^6-Naphthalene)bis(η^6-benzene)dichromium: (a) benzene, (b) naphthalene aa'bb' multiplet. (η^6-benzene)(η^6-naphthalene)chromium: (c) benzene, naphthalene peaks lost in base line, (d) solvent peaks, toluene-d_8, (e) spinning side bands, (f) THF with polymerized THF, (g) silicone from grease, (h) solvent impurity.

resonances" in the spectrum of the product consist of a singlet at 3.89 ppm for a complexed benzene and a single aa'bb' multiplet with groups of peaks at 3.97 and 5.67 ppm. Integration shows that these resonances are in the ratio benzene:aa'bb' = 12:8, suggesting that the "extra resonances" are from a compound containing two benzene units per naphthalene moiety. The naphthalene moiety appears as a single aa'bb' multiplet, indicating that its symmetry is similar to that of free naphthalene and, thus, that the benzene–chromium units must be symmetrically positioned around the bridgehead carbon atoms of the complexed naphthalene ligand (IX). The NMR data

IX
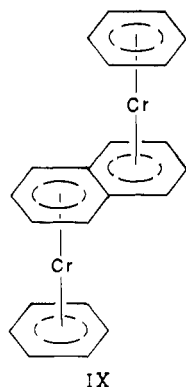
suggest that the product we initially called (η^6-benzene)(η^6-naphthalene)chromium is a mixture of two compounds, (η^6-benzene)(η^6-naphthalene)chromium and IX. This supposition was confirmed by studying the temperature dependence of the solubility of the mixture with NMR spectroscopy as an analytical technique.

Comparison of parts a and b of Figure 3 clearly shows the spectra of the two compounds. In Figure 3a, the predominant compound is (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium and has the symmetry of structure IX, while in Figure 3b, the preodminant compound is

(η^6-benzene)(η^6-naphthalene)chromium. The major difference in the samples used to obtain Figure 3a,b were the conditions used to synthesize the products (vide infra).

The new compound is best described as a slipped triple-decker sandwich species, e.g. IX, as opposed to the conventional triple-decker structure wherein the metal atoms are coaxial with the centers of the arene rings. It should be noted that in (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (and its analogues) the μ-naphthalene moiety is a contiguous aromatic system. Since these slipped triple-decker compounds are similar to a coaxial triple-decker sandwich, they should obey the same stability rules; indeed they do seem to obey the stable 34-electron count of Hoffmann et al.[24,25]

The substituents on the exchanged arene have a strong effect on the proportion of the slipped triple-decker formed. The electron-withdrawing substituents favor the formation of the slipped triple-decker compound while the electron-donating substituents favor the (η^6-arene)(η^6-naphthalene)chromium species. While no claims are made as to the absolute proportions of products (because of inevitable differences arising from the workup), the general trend is clear (Table I). In fact the slipped triple decker predominates with electron-withdrawing substituents (fluorobenzene) while only (η^6-arene)(η^6-naphthalene)-chromium is observed for the arenes carrying electron-donating substituents (hexamethylbenzene and tetralin).

We were interested to see that the previous report[6] on the synthesis of (η^6-arene)(η^6-naphthalene)chromium compounds did not include observations on the slipped triple-decker species. In an effort to clarify the situation the exchange procedure described in ref 6 was duplicated as closely as possible. Aside from a lack of purity, doubtlessly due to our interpretation of the procedure described in ref 6, a product distribution different from ours was observed. The NMR assay of the product synthesized by the procedure in ref 6 shows a double decker to slipped triple decker ratio of 25:1, (Figure 3b) whereas the assay on our procedures showed a sandwich to slipped triple decker ratio of 0.7:1 (Figure 3a). While these ratios depend to a minor extent on the workup of the reaction product, such a marked difference in the proportions can only be due to the conditions associated with the synthetic procedures. Specifically, the proportion of the THF used in the synthesis appears to effect the distribution and/or the rate of formation of the product species. The ligand exchange process occurs more rapidly and with enhanced formation of the slipped triple-decker compound when a greater proportion of THF is used, the reaction temperature being about 100 °C in both experiments.

An electronic problem arises when the standard electron count is considered for the triple-decker compounds. Granting effective η^6 bonding throughout for the naphthalene moiety leads to a 17-electron system for each chromium site, that is, half a stable 34-electron slipped triple decker.[24] According to conventional wisdom an additional two-electron donor ligand would be necessary to attain a stable 18-electron count. We were interested to learn if THF, which appears in the spectrum of (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (Figure 3a) could be supplying the "missing" two electrons. The ^{1}H NMR spectra obtained for numerous samples of (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium indicated no clear relationship between the amount of THF present and the amount of the slipped triple decker. Both the

(24) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

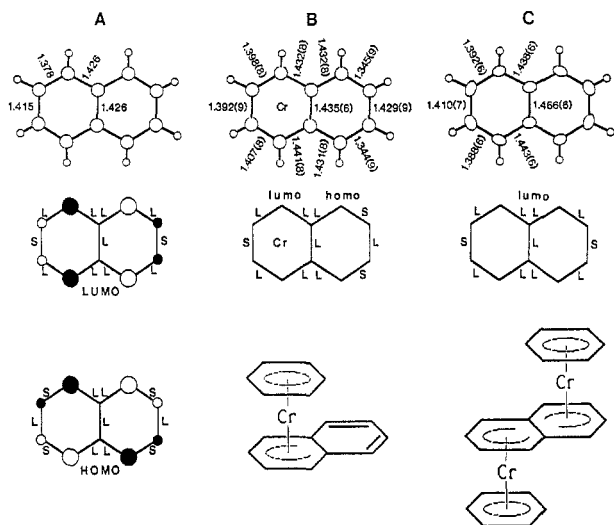(25) Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805.

Figure 4. (A) The bond lengths (esd = 0.002 Å) in crystalline naphthalene[27] with the molecular orbital diagrams for the HOMO and LUMO shown. The bonding π interactions should cause short (S) bond lengths, the antibonding π interactions long (L) bond lengths, and the nonbonding interactions long (L) bond lengths. (B) The bond lengths (Å) in the naphthalene moiety in benzene naphthalene chromium[6] with a qualitative description comparing the bond lengths of the naphthalene moiety to the HOMO and LUMO of crystalline naphthalene (A), which results in a molecular diagram wherein the unbound part of the naphthalene moiety has an overall butadiene-like character. (C) The bond lengths in the naphthalene moiety in $(\mu,\eta^6,\eta^6$-naphthalene)bis(η^6-benzene)dichromium with a qualitative description comparing the bond lengths of the naphthalene moiety to the LUMO of crystalline naphthalene (A), which results in a molecular diagram wherein the naphthalene moiety has an enhanced LUMO character.

sandwich compound and the slipped triple decker are present in THF-d_8 and in benzene-d_6 where the proportion of THF present is far too small to act as a ligand. That THF does not appear to play an important role in the product is emphasized by the lack of an organometallic fragment incorporating THF in any mass spectrum obtained; recall that all the samples are dissolved in THF (see Experimental Section) prior to mass spectral analysis. In a separate experiment, the THF contamination was removed by entrainment with benzene. Since both sandwich and slipped triple-decker compounds were clearly observed in this sample, we concluded that THF has no interaction with the slipped triple decker and that achieving the 18-electron count is unnecessary for stability.

These slipped triple-decker compounds conform to the theoretically stable 34-electron configuration of Hoffman et al.[24,25] Population of the naphthalene LUMO provides a rational for the differing reactivities of various arenes with respect to the exchange reaction. The electron-withdrawing arenes (e.g. fluorobenzene) help the naphthalene moiety take up electronic character resulting in the slipped triple decker being formed preferentially, whereas electron-donating arenes (e.g. hexamethylbenzene) disallow the formation of the slipped triple decker (see Table I). Insofar as the naphthalene moiety represents a contiguous aromatic system, its delocalized pπ-electron system would be expected to be distorted by chromium complexation.[26] This aromatic distortion is clearly visible in the proton coupling constants of the naphthalene moiety in the $(\mu,\eta^6,\eta^6$-naphthalene)bis(η^6-arene)dichromium com-

Scheme II
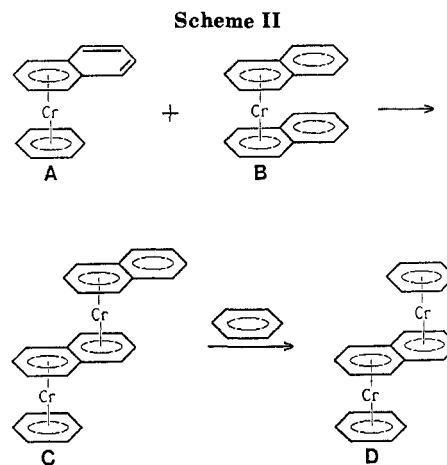
pounds (Table III). Although their multiplets are not completely resolved, their peak widths at half-height are indicative. This distortion results from the two ends of the naphthalene moiety carrying more electronic character than the central portion. Localization of bonding lessens the overall aromaticiity of the species, significantly reducing the bonding character between the naphthalene bridgehead carbons (Figure 4). As a consequence of the lack of pπ density on the naphthalene moiety's bridgehead carbon atoms, the projection of the chromium atoms onto the μ-naphthalene moiety's ring centroids is displaced by 0.053 (2)Å toward the higher pπ density on the ends of the naphthalene moiety.

Perhaps more interesting than the extent of localization of bonding in the naphthalene moiety is the process through which the slipped triple decker came to be formed. With the simple aromatic compounds, having symmetric p character, double ligand exchange with bis(η^6-naphthalene)chromium to form the bis(η^6-arene)chromium has not previously been reported. The (η^6-arene)(η^6-naphthalene)chromium compounds exhibit structure and reactivity reminiscent of the bis(η^6-arene)chromium compounds (i.e., they do not exchange the remaining naphthalene moiety); thus it is not likely that the slipped triple-decker compounds result from the combination of the (η^6-arene)(η^6-naphthalene)chromium molecules. Rather it appears that the combination of (η^6-arene)(η^6-naphthalene)chromium (A) with bis(η^6-naphthalene)-chromium (B) to form a $(\mu,\eta^6,\eta^6$-naphthalene)(η^6-arene)(η^6-naphthalene)dichromium intermediate (C), which undergoes further ligand exchange forming the $(\mu,\eta^6,\eta^6$-naphthalene)bis(η^6-arene)dichromium slipped triple-decker (D) species, is more likely (Scheme II). Thus the uncomplexed part of the naphthalene moiety in an (η^6-arene)(η^6-naphthalene)chromium compound is a special sort of arene, being a distorted pπ system, which can complex to chromium in an incomplete manner.

The result of preliminary experiments support these suggestions.

Dimethyldiphenylsilane reacted with bis(η^6-naphthalene)chromium in THF to yield (η^6-dimethyldiphenylsilane)(η^6-naphthalene)chromium and the double exchanged species bis(η^6-dimethyldiphenylsilane)chromium as a minor product; interestingly the slipped triple decker was not found. This observation suggests that the silicon center allows the incomplete association of the arene moiety after the first exchange,[28] allowing the second exchange to occur. Thus the silyl ligand acts as its own catalyst for exchange, perhaps in much the same manner

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as the distorted and uncomplexed half of the complexed naphthalene moiety in the formation of a $(\mu,\eta^6,\eta^6$-naphthalene)$(\eta^6$-arene)$(\eta^6$-naphthalene)dichromium intermediate.

Registry No. I, 33085-81-3; IX, 108058-60-2; $(\eta^6$-naphthalene)$(\eta^6$-fluorobenzene)chromium, 108008-83-9; $(\eta^6$-naphthalene)$(\eta^6$-benzene)chromium, 99537-72-1; $(\eta^6$-naphthalene)$(\eta^6$-toluene)chromium, 108008-84-0; $(\eta^6$-napthalene)$(\eta^6$-mesitylene)chromium, 99537-74-3; $(\eta^6$-naphthalene)$(\eta^6$-hexamethylbenzene)chromium, 99537-75-4; $(\eta^6$-naphthalene)$(\eta^6$-tetralin)benzene, 108008-85-1; $(\eta^6$-naphthalene)$(\eta^6$-dimethyldiphenylsilane) chromium, 108008-82-8; $(\mu,\eta^6,\eta^6$-naphthalene)bis$(\eta^6$-fluorobenzene)dichromium, 108058-59-9; $(\mu,\eta^6,\eta^6$-naphthlene)bix$(\eta^6$-toluene)dichromium, 108081-57-8; $(\mu,\eta^6,\eta^6$-naphthalene)bis$(\eta^6$-mesitylene)dichromium, 108058-61-3; bis$(\eta^6$-dimethyldiphenylsilane)chromium, 108008-86-2; bix$(\eta^6$-tetralin)chromium, 93646-21-0; naphthalene, 91-20-3.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and least-squares planes and dihedral angles (3 pages). Ordering information is given on any current masthead page.

Syntheses and Structural Comparison of the η^6-Arene Complexes Sm(C₆Me₆)(AlCl₄)₃ and U(C₆Me₆)(AlCl₄)₃

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The mononuclear complexes M(C₆Me₆)(AlCl₄)₃ of U(III), 1, and Sm(III), 2, have been prepared and structurally characterized. Although their crystals are not isomorphous because of solvent molecules in the crystal lattice of 2, the molecular complexes are isostructural and therefore permit a meaningful comparison of the geometrical properties of an actinide and a lanthanide arene complex. U(C₆Me₆)(AlCl₄)₃ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.816$ (5) Å, $b = 17.918$ (8) Å, $c = 9.730$ (4) Å, $\alpha = 96.09$ (3)°, $\beta = 118.91$ (3)°, $\gamma = 80.98$ (3)°, $V = 1479$ (2) Å³, and $Z = 2$. Crystals of Sm(C₆Me₆)(AlCl₄)₃·1.5C₇H₈ belong to the monoclinic crystal class, space group $P2_1/c$, with $a = 18.696$ (4) Å, $b = 16.906$ (3) Å, $c = 12.262$ (2) Å, $\beta = 100.8$ (2)°, $V = 3807$ (2) Å³, and $Z = 4$. In general, comparable M–ligand bond lengths reflect the difference in the ionic radii of uranium and samarium. This suggests that the acceptor orbitals are comparable in the actinide and the lanthanide complexes and that, consequently, f orbitals are not substantially involved in arene bonding.

Introduction

There is now ample evidence that arene derivatives of f-block elements are surprisingly stable compounds in that structurally characterized examples of U(III),[1,2] U(IV),[3,4] and Sm(III)[5] are available. The η^6-coordination of the neutral arenes leaves no doubt that thermodynamically stable dative π-bonds can be formed with f elements, albeit, as the samarium complex would suggest, without significant participation of f orbitals.

When Sm(hmb)(AlCl₄)₃ (2) was found to be structurally related to a previously reported benzene complex of U(III), U(C₆H₆)(AlCl₄)₃ (3),[1] we decided to pursue the synthesis of the mononuclear hmb derivative of U(III) in order to evaluate the structural changes that occur upon lanthanide vs. actinide substitution in arene complexes. The above-mentioned benzene complex 3 appeared unsuitable for this purpose because we had observed that steric interactions

of the methyl substituents play an important role in determining the structural details of the samarium complex. More importantly, the benzene ring in compound 3 had not been included in the refinement but rather was fitted to the Fourier map with idealized geometry.

We have now prepared a homologous pair of hmb complexes of Sm(III) and U(III) which allows a meaningful comparison of the structural data.

Experimental Section

All preparations were performed in an atmosphere of purified argon in Schlenk-type glassware. Solvents were distilled under N₂ from appropriate drying agents and transferred with syringes. AlCl₃ was sublimed prior to use. SmCl₃ (Alfa) and hmb (Kodak) were used as received. UCl₄ was prepared by published procedures.[6]

Preparation of M(hmb)(AlCl₄)₃ (M = U, Sm). In a typical experiment 1 mmol of the respective metal halide (SmCl₃, UCl₄), 405 mg (2.5 mmol) of hmb, and 1 g (7.5 mmol) of AlCl₃ were boiled under reflux in toluene for ca. 30 min before 100 mg of aluminum foil (in strips) was added from a side-arm flask. The foil had previously been cleaned with acetone and CH₂Cl₂. Reflux was continued for 5 h during which time a color change to blood red (Sm) or maroon (U) occurred. The solutions were filtered hot

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