Nucleophilic Aromatic Substitutions: Hydrodealkoxylation, Hydrodehalogenation, and Hydrodeamination of Alkoxy, Halogeno, and Amino (η^6-Arene)tricarbonylchromium Complexes

Jean-Pierre Djukic, Francoise Rose-Munch, Eric Rose,* and Frederic Simon

Laboratoire de Chimie Organique, URA 408, Universite Pierre et Marie Curie, Case 181, 4, place Jussieu, 75252 Paris Cedex 05, France

Yves Dromzee

Laboratoire de Chimie des Metaux de Transition, Universite Pierre et Marie Curie, Batiment F, 4, place Jussieu, 75252 Paris Cedex 05, France

Hydrodealkoxylation, -dehalogenation, and -deamination, occur while lithium triethylborohydride is added to [η^6-alkoxy-, halogeno-, and -(dimethylamino)benzene]tricarbonylchromium complexes. In the case of (η^6-benzene)tricarbonylchromium, addition of deuteride to the benzene ring gives reversibly an anionic tricarbonyl(η^5-cyclohexadienyl)chromium complex which can be trapped by triphenyltin chloride to yield the neutral binuclear complex (η^5-C_6H_6D)(CO)$_3$Cr–Sn(C_6H_5)$_3$. The latter complex molecular structure has been confirmed by single-crystal X-ray diffraction analysis. Empirical formula $C_{27}H_{21}DCrO_3Sn$: triclinic system, space group $P1$, $z = 2$, $a = 8.961(4)$ Å, $b = 10.853(5)$ Å, $c = 12.713(2)$ Å, $\alpha = 85.15(3)°$, $\beta = 86.26(2)°$, $\gamma = 72.40(4)°$, $R = 0.033$, $Rw = 0.037$ (unit weight).

Introduction

(η^6-Arene)tricarbonylchromium complexes play an important role in organometallic chemistry, which stems from their particular reactivity as it has been described in numerous reviews.[1] Their easy preparation has promoted series of studies of their ability to form stabilized benzylic anions[2–4] and cations,[3] to react in various ways with nucleophiles,[4] to be easily metalated,[5] and to be active catalysts in hydrogenation reactions.[6]

Our research is mainly oriented toward the application of these π-arene–metal complexes in organic synthesis as well as in the mechanistic study of their reactions with nucleophiles and electrophiles. For instance, in the case of chiral complexes, we have recently described the asymmetric formation and the resolution of ortho-substituted (η^6-benzaldehyde)tricarbonylchromium complexes,[7] and in the case of alkoxy and halogeno (η^6-arene)tricarbonylchromium complexes, we have described the cleavage of aromatic carbon–oxygen[8] and carbon–halogen[9,10] bonds by carbon nucleophiles via ipso, cine,[9a] and tele[8b] nucleophilic aromatic substitutions (S_NAr). We decided to undertake the complete study of the

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reactivity of (η^6-arene)tricarbonylchromium complexes vs noncarbanionic nucleophiles such as H$^-$ in order to shed light on the mechanism of the hydride nucleophilic aromatic substitution reaction (S$_N$Ar).

Hydride addition to cationic π-arene–metal complexes occurs readily in the case of complexes such as [(η^6-arene)M(CO)$_3$]$^+$ (M = Mn,[11a–e] Re[11f,g]), [(η^6-arene)]Mn-(CO)$_2$L]$^+$,[12] (L = CH$_3$CN, PR$_3$), [(η^6-arene)(η^5-cyclopentadienyl)Fe]$^+$,[13] [(η^6-arene)V(CO)$_4$]$^+$,[14] [(η^6-arene)Cr(CO)$_2$NO]$^+$,[15] [(η^6-arene)$_2$M]$^{2+}$ (M = Fe,[16a,b] Ru[16a,c,d]), and [(η^6-arene)(η^5-pentamethylcyclopentadienyl)Ir]$^{2+}$,[17] the major products obtained being neutral or monocationic η^5-cyclohexadienyl complexes. In the case of chromium derivatives, we recently reported that hydrides such as LiEt$_3$BH react with alkoxy,[18a,d] halogeno,[18b] and dimethylamino[18c] arenetricarbonylchromium complexes via ipso, cine, and tele nucleophilic aromatic substitution. Herein, we report the full details of this study[19] along with further explorations of the chemistry of tricarbonyl-(η^5-cyclohexadienyl)chromium complexes.

Results and Discussion

Preparation of Complexes. (η^6-Arene)tricarbonylchromium complexes were synthesized by using the standard procedure of thermolysis of Cr(CO)$_6$ in presence of the free arenes.[20] Purification by flash chromatography and recrystallization afforded air-stable yellow

Table 1. Products Obtained by Addition of a Hydride to Alkoxy- or Methoxyarene Tricarbonylchromium Complexes

(a) LiEt$_3$BH; (b) LiEt$_3$BD; (e) HCl; (f) CF$_3$CO$_2$H–THF; (h) H$_2$O

substrate	OR$_1$	R$_2$	Y$^-$	H$^+$	products	Y	yield (%)	entry
1	m-OMe	Et	a	e or f	**2a**	H	100	1
1	m-OMe	Et	b	e or f	**2b**	m-D	100	2
3a	o-OMe	SiMe$_3$	a	f	**4**	H	71	3
3b	o-OPh	SiMe$_3$	a	f	**4**	H	76	4
3a	o-OMe	SiMe$_3$	b	f	**4-p**	p-D	71	5
3b	o-OPh	SiMe$_3$	b	f	**4-p**	p-D, o-D	76	6
5	o-OPh	Me	a	f	**6**	H	55	7
7a	o-OMe	^{t}Bu	a	h	**8**	H	34	8
7b	m-OMe	^{t}Bu	a	h	**8**	H	66	9
7c	p-OMe	^{t}Bu	a	h	**8**	H	83	10
7a	o-OMe	^{t}Bu	b	f or h	**8-o**	o-D	34	11
7b	m-OMe	^{t}Bu	b	f	**8-m, 8-p**	m-D, p-D	77 (84:16)	12
7c	p-OMe	^{t}Bu	b	f or h	**8-p**	p-D	83	13

crystals of complexes **1, 7a, 7b, 7c, 9, 13, 14, 15, 16, 18**,[8c] and **23**.[9d] Complexes **3a, 3b, 5**,[8c] **20, 22**, and **29**[9f] were obtained by lithiation of [η^6-chloro-, -fluoro-, -phenoxy- or -(N,N-dimethylamino)benzene]tricarbonylchromium with n-BuLi followed by treatment with an electrophile (Me$_3$SiCl, (i-Pr)$_3$SiCl, MeI).

^{1}H and ^{13}C NMR Spectra.[21] The ^{1}H and ^{13}C NMR spectra of the new complexes showed the usual upfield shift of the aromatic proton and carbon resonances with respect to those of the corresponding free arenes. Spectra were assigned through a combination of peak multiplicities, chemical shifts, coupling constants analyses, and ^{13}C–^{1}H two-dimensional correlation experiments. Complete data are reported in the experimental section.

Addition of Lithium Triethylborohydride to Alkoxy and Aryloxy Arenetricarbonylchromium Complexes. LiEt$_3$BH was added to a refluxing THF solution of (η^6-3-ethylanisole)Cr(CO)$_3$ (**1**). After refluxing the reaction mixture for 2 h and treating the solution with aqueous HCl, (η^6-ethylbenzene)Cr(CO)$_3$ (**2a**) was recovered quantitatively (Table 1, entry 1). In order to determine the regioselectivity of the addition of this hydride to the arene ring, we undertook the same experiment with LiEt$_3$BD. Thus, complex **1** yielded quantitatively (η^6-3-(deuterioethyl)benzene)Cr(CO)$_3$, complex **2b** (Table 1, entry 2).

Knowing that cine[9a] and/or tele[8] nucleophilic aromatic substitution could occur by adding a carbon nucleophile to a chromium complex, the last experiment (Table 1, entry 1) could not ascertain whether the hydride added on the carbon bearing the methoxy group (ipso addition) or on the carbon meta to the methoxy group (tele–meta addition).[8a] Consequently, we undertook the study of the reaction of complex **1** with LiEt$_3$BD by ^{1}H NMR spectroscopy. Addition of a THF-d_8 solution of LiEt$_3$-BD (2 equiv) to complex **1** at room temperature led, without any acidic treatment, to the slow in situ formation of the deuterated ethylbenzene complex. This proves that the displacement of the methoxy group occurred via an ipso S$_N$Ar process. These results provide relevant information about the capability of

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hydride to add at a substituted position of the complexed arene although it is strongly disfavored by steric and electronic interactions.

We decided to carry out further investigations on the regioselectivity of the hydride addition in the case of ortho-disubstituted complexes. [η6-2-(Trimethylsilyl)-anisole]Cr(CO)3 (**3a**) was chosen. Treatment of **3a** with LiEt3BD, followed by acidification of the reaction medium yielded [η6-4-deuterio(trimethylsilyl)benzene]Cr-(CO)3 (**4-p**; 71% yield) (Table 1, entry 5). In order to see whether this reaction could occur in the case of phenoxy-substituted derivatives, we carried out the same experiment with (η6-2-methylphenoxybenzene)Cr-(CO)3 (**5**) and we obtained (η6-toluene)Cr(CO)3 (**6**; 55% yield) (Table 1, entry 7). [η6-2-(Trimethylsilyl)phenoxy-benzene]Cr(CO)3 (**3b**) reacted with LiEt3BH at 67 °C for 24 h to yield, after CF3CO2H treatment, the (tri-methylsilyl)benzene derivative **4** (76% yield) (Table 1, entry 4). When a deuteride source was used, the ratio between the deuterio isomers was easy to determine by 1H NMR spectroscopy; in all cases the para-deuterated isomer **4-p** (tele–meta SNAr product) was the major product even though contaminated with the ortho-deuterated isomer **4-o** (15-25%) (Table 1, entry 6). (η6-*tert*-Butylanisole)Cr(CO)3 (**7a**) reacted with LiEt3BD (2 equiv) in THF at 67 °C for 18 h and yielded, after CF3-CO2H treatment or hydrolysis, the ortho-deuterated *tert*-butylbenzene derivative **8-o** (34% yield) along with the starting complex (60% recovered) (Table 1, entry 11). With the meta isomer **7b**, using similar experimental procedures, complexes **8-m** and **8-p** were obtained in a ratio of 84:16 (77% overall yield) after CF3COOH treatment (entry 12). With the para isomer **7c**, the reaction with LiEt3BD followed by a CF3COOH treatment or hydrolysis led to the complex **8-p** only (83% yield) (entry 13).

It is worth noting that if complex **7c** is treated at room temperature for 1 h with LiEt3BD and the resulting medium with CF3CO2H (5 equiv), the major product is the ortho-deuterated *tert*-butylbenzene derivative **8-o**, the starting complex **7c** being recovered in large amounts (**8-o**:**8-p**:**7c** = 21:7:72). After 6 h at room temperature, the ratio **8-o**:**8-p**:**7c** is 8:40:52. This clearly indicates the reversible character of the hydride addition and means that formation of the para isomer is favored at longer reaction times vs that of the ortho isomer. The evolution of the reaction medium composition was easy to follow by 1H NMR, after treatment of aliquots with CF3CO2H, since the aromatic protons of the *tert*-butyl-benzene derivative produced resonate at very different fields. These results are reproduced in Figure 1. If LiEt3BD (2 equiv) and CF3CO2H (5 equiv) are used, **8-p** is obtained in 83% yield (Table 1, entry 13).

Scheme 1 displays a mechanism for the reversible addition of hydride to an unsubstituted position at the complexed ring. Compound **8-o**, which is favored early in the reaction, results from the protonation of an anionic η5-cyclohexadienyl intermediate formed from the reversible addition of deuteride at the meta position with respect to the methoxy group. The latter evolves by successive isomerizations involving putative fluxional chromium–hydride species[16d,22] that give ultimately, after MeOH elimination, the rearomatization product **8-o**. As proposed elsewhere, the rearomatization process can be the driving step of this process that allows
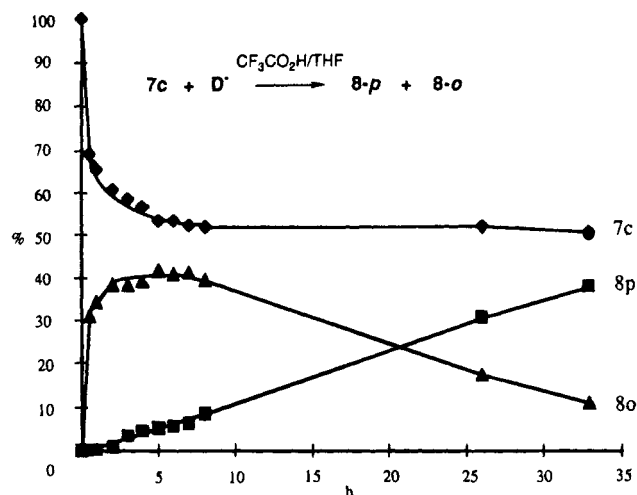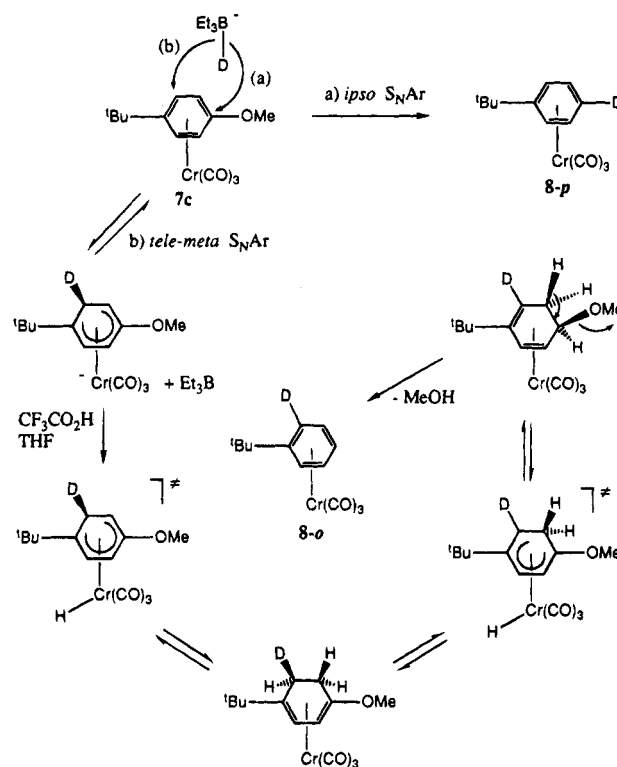

Figure 1. Addition of LiEt3BD to **7c** (1:1): evolution of the reaction medium composition (molar percent) after quenching with CF3CO2H vs time.

Scheme 1

the recovery of an arene–chromium complex without loss of the tricarbonylchromium moiety.[8c] Several groups[4d,23-25] noticed that under kinetic control the electronic effects of the arene substituents can influence the regiochemistry of nucleophilic additions. But we have proposed[25a] that the conformation of the Cr(CO)3 tripod can control the regiochemistry of the nucleophilic

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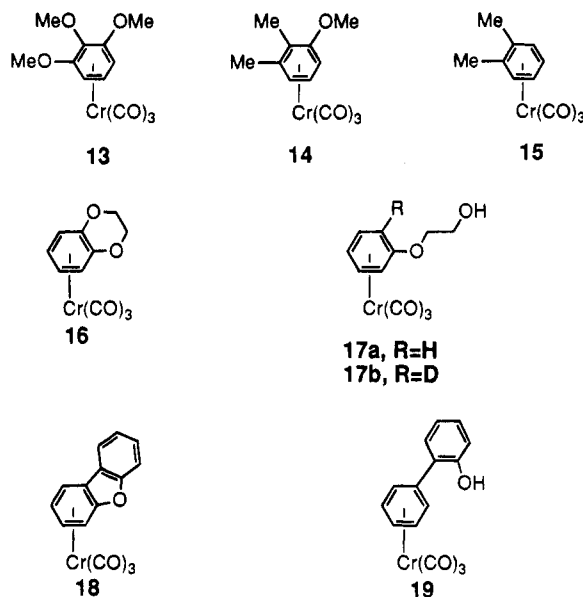(23) Semmelhack, M. F.; Clark, G.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.* **1979**, *101*, 217.

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attack so that Cr—CO bond eclipsed positions at the arene ring are favored. Thus, in the case of complex **7c**, it is reasonable to define the anionic η^5-cyclohexadienyl adduct as the kinetic product of the addition of D$^-$ as well as the precursor of **8-o**, which is created by the subsequent protonation—elimination reaction. Under similar experimental conditions, the three complexes **7a**, **7b**, and **7c** yielded only the ipso S$_N$Ar products **8-o** (34% yield), **8-m** (66% yield) and **8-p** (83% yield) along with the corresponding starting complexes when the reaction media were hydrolyzed with acidic water rather than treated with a solution of trifluoroacetic acid in tetrahydrofuran (Table 1, entries 8—10).

We decided to study these alkoxy and aryloxy group displacement reactions with different trisubstituted complexes and particularly with trimethoxyarene derivatives. In the case of (η^6-1,3,5-trimethoxybenzene)-Cr(CO)$_3$ (**9**), it was not necessary to heat the reaction mixture. Even at room temperature, it was possible to monodemethoxylate the arene ring, the major product being (η^6-1,3-dimethoxybenzene)Cr(CO)$_3$ (**10a**) (**10b** for the 5-deuterio analog of **10a**, 73% yield, eq 1). Of course, heating the reaction mixture with an excess of hydride yielded quantitatively (η^6-benzene)Cr(CO)$_3$ (**12**) (this reaction occurs with LiAlH$_4$ as well).
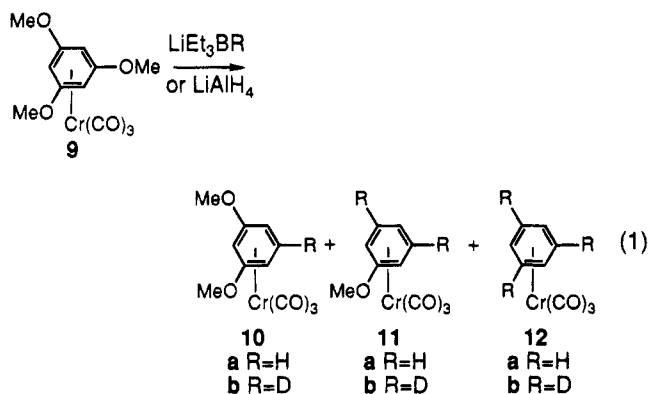

In the case of the trisubstituted trimethoxyarene complex **13**, the major product can be the anisole derivative **11a**. Indeed, treatment of (η^6-1,2,3-trimethoxybenzene)Cr(CO)$_3$ (**13**) with an excess of LiEt$_3$BD yielded as major products the dideuterated anisole derivatives respectively deuterated at the 2, 6 and 2, 3 positions. Similarly, treatment of (η^6-2,3-dimethylanisole)Cr(CO)$_3$ (**14**) with LiEt$_3$BH yielded the o-xylene complex **15** (47% yield). Complexed phenyl-substituted oxygenated heterocycles were studied in order to verify the possibility of ring-opening reactions by a hydride treatment. For instance, (η^6-benzodioxane)Cr(CO)$_3$ (**16**) underwent ring opening when treated with LiEt$_3$BH, yielding a mixture of **17a** (33% yield) and **12a** (10% yield). LiEt$_3$BD treatment afforded, via an ipso S$_N$Ar, the complex **17b** deuterated at the position ortho to the ether group. In addition, we noticed that no nucleophilic addition oc-

(25) (a) Boutonnet, J. C.; Mordenti, L.; Rose, E.; Le Martret, O.; Precigoux, G. *J. Organomet. Chem.* **1981**, *221*, 147. (b) Uemura, M.; Minami, T.; Shinoda, Y.; Nishimura, H.; Shiro, M.; Hayashi, Y. *J. Organomet. Chem.* **1991**, *406*, 371. (c) The protons meta to the amino group resonate at the lowest field 5.69 ppm in CDCl$_3$ and the anti eclipsed ortho protons resonate at higher field (4.68 ppm in CDCl$_3$). The ortho and meta protons of the corresponding free arene resonate respectively at 6.73 and 7.27 ppm in CDCl$_3$; it is worth noting the relatively stronger shielding of the noneclipsed aromatic protons (2.05 ppm) vs that of the eclipsed protons (1.58 ppm).
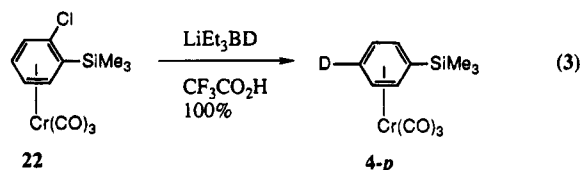

curred on the ethylene fragment. Another example was obtained with the dibenzofuran complex **18**. Using the same experimental procedure, we isolated complex **19** (75% yield).

Addition of Lithium Triethylborohydride to (η^6-Halogenoarene)Cr(CO)$_3$ Complexes. Addition of deuteride to [η^6-2-fluoro(triisopropylsilyl)benzene]Cr-(CO)$_3$ (**20**) at −78 °C followed by CF$_3$CO$_2$H treatment gave a red solution which slowly became yellow (eq 2).
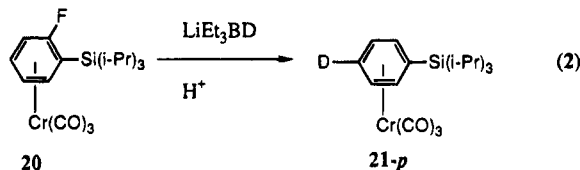
After recrystallization, [η^6-4-deuterio(triisopropylsilyl)-benzene]Cr(CO)$_3$ (**21-p**) was obtained via a tele—meta S$_N$Ar reaction (86% yield). When water was used instead of CF$_3$CO$_2$H, complex **21-p** was recovered in 60% yield. Similar experiments carried out with the trimethylsilyl analog of **20** yielded not only the hydrodefluoration product but also some benzene complex resulting from the displacement of both the fluoride and trimethylsilyl groups induced by the CF$_3$CO$_2$H treatment.

We undertook the study of the behavior of hydrides toward [η^6-2-chloro(trimethylsilyl)benzene]Cr(CO)$_3$ (**22**); trimethylsilylbenzene derivative **4-p**, deuterated at the para position via a tele—meta S$_N$Ar was obtained quantitatively (eq 3). In the case of p-chlorotoluene

derivative **23**, LiAlD$_4$ reacted at room temperature to yield quantitatively, after CF$_3$CO$_2$H treatment, toluene derivatives **6-o** and **6-m** respectively deuterated at the ortho and meta positions (34:66) according to NMR spectra, via cine and tele—meta S$_N$Ar (Table 2, entry 1). Using LiEt$_3$BD instead of LiAlD$_4$ (Table 2, entry 2),

**Table 2. Products Obtained by Addition of a Hydride to Halogenoarene Tricarbonylchromium Complexes**
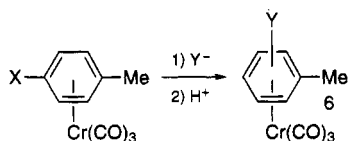
(b) LiEt$_3$BD; (d) LiAlD$_4$; (f) CF$_3$CO$_2$H−THF; (g) CF$_3$CO$_2$D−THF; (h) H$_2$O

substrate	X	Y$^-$	H$^+$	products	Y	yield (%)	entry
23	Cl	d	f	6-o, 6-m	o-D, m-D	100	1
23	Cl	b	f	6-m	m-D	100	2
23	Cl	b	g	6-o, 6-m	o-, m-D$_2$	100	3
24	F	b	h	6-p	p-D	100	4

unexpectedly only 3-deuteriotoluene, complex **6-m**, was obtained in quantitative yield. Using LiEt$_3$BD and CF$_3$-CO$_2$D, the 2,3-dideuteriotoluene complex **6-o**, -**m** was produced in good agreement with a cine S$_N$Ar process[9a] (Table 2, entry 3). In the case of the p-fluorotoluene complex **24**, LiEt$_3$BD addition followed by water treatment yielded (η^6-4-deuteriotoluene)Cr(CO)$_3$ **6-p** (70% yield) (Table 2, entry 4).

Addition of Lithium Triethylborohydride to N,N-Dimethylaniline Derivatives. We investigated the regioselectivity of the hydride addition in the case of disubstituted aniline complexes as [η^6-(N,N-dimethyl-amino)anisole]Cr(CO)$_3$ (**25**). Addition of LiEt$_3$BH at room temperature followed by CF$_3$CO$_2$H treatment afforded unexpectedly two complexes, namely the anisole and N,N-dimethylaniline complexes, **11** and **26a**, in 34% and 24% yield, respectively (eq 4). The formation of a
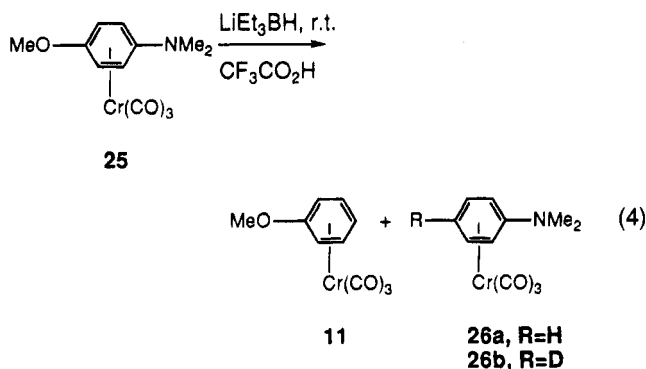
N,N-dimethylaniline derivative was expected as a result of a carbon−oxygen cleavage. On the other hand, the scission of the carbon−nitrogen bond was unexpected. Therefore, we undertook the systematic study of a series of (N,N-dimethylamino)benzene derivatives.

Addition of a large excess of LiEt$_3$BH to **26a** followed by CF$_3$CO$_2$H treatment at room temperature gave a red solution which became rapidly yellow. Extraction and purification yielded (η^6-benzene)Cr(CO)$_3$ complex (**12**) and the starting complex.

Reaction of LiEt$_3$BD with [η^6-2-methyl-(N,N-dimethyl-amino)benzene]Cr(CO)$_3$ (**27a**) gave after CF$_3$CO$_2$H treatment at room temperature the toluene complexes **6-o** and **6-m** deuterated at the 2 or 3 position in a ratio 40: 60 (only 23% overall yield of toluene derivatives due to decomposition problems) (Table 3, entry 1). In order to improve the yield of the latter reaction, we undertook the same experiment using the stronger acid CF$_3$SO$_3$H, but unfortunately, the yield remained identical. In the case of the meta isomer **27b**, we obtained the toluene

Table 3. Products Obtained by Addition of a Hydride to Anilinetricarbonylchromium Derivatives
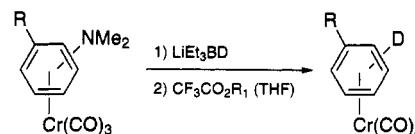
substrate	R	R$_1$	products	D	yield (%)	entry
27a	o-Me	H	6-o, 6-m	o-D, m-D	23 (40:60)	1
27b	m-Me	H	6-o, 6-m or 6-p	o-D, m-D or p-D	8 (25:75)	2
28	p-^{t}Bu	H	8-o, 8-m	o-D, m-D	8 (94:6)	3
29a	Σ-SiMe$_3$	H	4-o, 4-p	o-D, p-D	56 (84:16)	4
29b	m-SiMe$_3$	H	4-p	p-D	61	5
29b		D	4-m, - p	m-, p-D$_2$	60	6

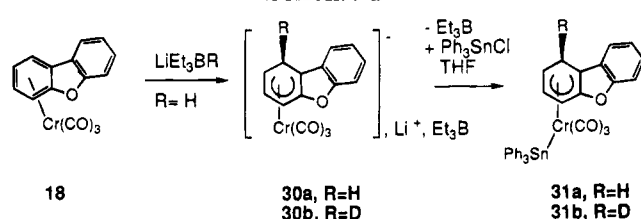derivatives **6-o** or **6-p** and **6-m** in 8% yield (**6-o** or **6-p**: **6-m** = 25:75) (Table 3, entry 2).

We carried out a similar experiment with another complex having a well-defined conformation for the tricarbonyl moiety.[25a] Indeed it is well-known that electron donor groups are usually eclipsed by a chromium carbonyl bond and that sterically demanding groups such as tert-butyl group are anti-eclipsed by a chromium carbonyl bond.[26] The major conformer of [η^6-4-tert-butyl-(N,N-dimethylamino)benzene]Cr(CO)$_3$ certainly has the N,N-dimethylamino group eclipsed by a Cr−CO bond.[25c] In the case of complex **28**, reaction with LiEt$_3$BD followed by CF$_3$CO$_2$H treatment yielded (η^6-3-deuterio-tert-butylbenzene)Cr(CO)$_3$ (**8-m**) and (η^6-2-deuterio-tert-butylbenzene)Cr(CO)$_3$ (**8-o**) in the ratio **8-o**: **8-m** = 94:6 (8% yield) (Table 3, entry 3). The formation of the major isomer is in good accord with a tele−meta S$_N$Ar mechanism in which hydride addition occurs at a carbon eclipsed by a chromium−carbonyl bond. This is in good agreement with the fact that nucleophilic carbanions add reversibly to (η^6-arene)Cr(CO)$_3$ complexes mainly at a carbon eclipsed by a chromium carbonyl bond, at low temperature, under kinetic control.[25a,26,28] We extended this study of the regioselectivity of the hydride addition on other well conformationally defined complexes bearing a trimethylsilyl group. Under the experimental conditions previously described, the treatment of [η^6-2-(trimethylsilyl)-(N,N-dimethylamino)benzene]Cr(CO)$_3$ (**29a**) yielded a mixture of 2- and 4-deuterio derivatives of [η^6-(trimethylsilyl)-benzene]Cr(CO)$_3$, **4-o** and **4-p**, in 56% yield (ratio **4-o**: **4-p**:84:16 determined by ^{1}H NMR spectroscopy) (Table 3, entry 4). We suggest that the two products were obtained as a result of a tele−meta S$_N$Ar reaction, the ipso S$_N$Ar path being very unlikely. With the meta-disubstituted derivative **29b**, the experiment carried out under the same conditions gave only the 4-deuterio-(trimethylsilyl)benzene derivative, **4-p**, which was obtained via a cine S$_N$Ar (61% yield) (Table 3, entry 5). Knowing that, in the case of a cine S$_N$Ar, the deuterium of CF$_3$CO$_2$D is incorporated in the aromatic ring, we

(26) Semmelhack, M. F.; Garcia, J. L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467.

(27) (a) Solladie-Cavallo, A.; Suffert, J. *J. Org. Magn. Res.* **1980**, *14*, 426. (b) Boutonnet, J. C.; Levisalles, J.; Rose, E.; Precigoux, G.; Courseille, C.; Platzer, N. *J. Organomet. Chem.* **1983**, *255*, 317. (c) Boutonnet, J. C.; Levisalles, J.; Rose-Munch, F.; Rose, E. *J. Organomet. Chem.* **1985**, *295*, 153.

(28) (a) Ohlsson, B.; Ullenius, C. *J. Organomet. Chem.* **1984**, *267*, C34. (b) Kundig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (c) Kundig, E. P.; Desobry, V.; Simmons, D. P.; Wenger, E. *J. Am. Chem. Soc.* **1989**, *111*, 1804. (d) Ohlsson, B.; Ullenius, C.; Jagner, S.; Grivet, C.; Wenger, E.; Kundig, E. P. *J. Organomet. Chem.* **1989**, *365*, 243. (e) Rose-Munch, F.; Rose, E.; Semra, A.; Bois, C. *J. Organomet. Chem.* **1989**, *363*, 103.

Scheme 2

18　　　　　**30a, R=H**　　　　**31a, R=H**
　　　　　　　　30b, R=D　　　　**31b, R=D**

Scheme 3

32a　　　**34**　　　**12**　　　**35**

Scheme 4

12　　**32a, R= H**　　**33a, R= H**
　　　　32b, R= D　　**33b, R= D**

studied the reaction using LiEt$_3$BD and CF$_3$CO$_2$D and obtained, as expected, the 3,4-dideuterated trimethylsilylbenzene derivative, **4-m**, **-p** (entry 6).

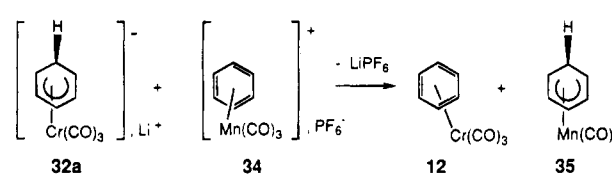**Tricarbonyl(η^5-cyclohexadienyl)chromium Complexes.** Although the parameters that drive the kinetic control of nucleophilic attack on (η^6-arene)tricarbonylchromium complexes are rather well understood, there is a lack of data for the factors determining thermodynamically controlled reactions. These latter reactions are mainly driven by the stability of the adducts, e.g., the anionic tricarbonyl(η^5-cyclohexadienyl)chromium complexes.[26,28a,28c] The stability of such intermediates is likely to be determined by the electronic distribution and steric interactions. We were interested in investigating a few (η^5-cyclohexadienyl) complexes in order to understand their properties.

We reported previously that the addition of LiEt$_3$BR on (η^6-dibenzofuran)Cr(CO)$_3$ yielded, after the removal of both Et$_3$B and solvents, the anionic adducts **30a** and **30b** as yellow amorphous powders (Scheme 2).[19] The same reaction carried out for 48 h afforded, after hydrolysis, the biphenyl derivative **19** resulting from the cleavage of the C$_{Ar}$—O bond via an ipso S$_N$Ar reaction. The anionic intermediates **30** trapped with Ph$_3$SnCl gave the bimetallic complexes **31**; single-crystal X-ray diffraction of **31a** provided the first molecular structure of a hetero-disubstituted tricarbonyl(η^5-cyclohexadienyl)triphenyltinchromium(II) (Sn—Cr) complex.[19]

The ^{13}C NMR (CDCl$_3$, 50 MHz) spectrum, performed at room temperature, showed a large unresolved signal in the carbonyl resonance zone at approximately 231 ppm.[19] At low temperature (213 K), a ^{13}C NMR experiment (75 MHz) carried out in the same solvent revealed three well-defined resonances at 238.87, 230.73 and 223.76 ppm, accounting for the three differentiated carbonyl ligands. This indicates that, on the NMR time scale at this temperature, the triphenyltintricarbonylchromium moiety rotates very slowly. Unfortunately, we were not able to observe the coalescence of these signals at higher temperatures in part because of an important line-broadening effect and mainly because of decomposition. Variable-temperature ^{1}H NMR experiments monitored from 213 to 343 K did not show any significant temperature-related shifts of the resonances of the main complex **31**.

The formation of complex **30a** is the result of the reversible addition of hydride on complex **18**. Indeed, it undergoes an isomerization at longer reaction times that leads to C$_{Ar}$—O bond ipso cleavage and the formation of complex **19**. This isomerization is likely to be caused by the triethylborane released from the reaction of LiEt$_3$BH with the starting complex **18**. A further evidence of the reversibility of the hydride addition is given by the hydride transfer reaction occurring stoichiometrically between the pure anionic complex **32a** and the cationic (η^6-benzene)tricarbonylmanganese com-
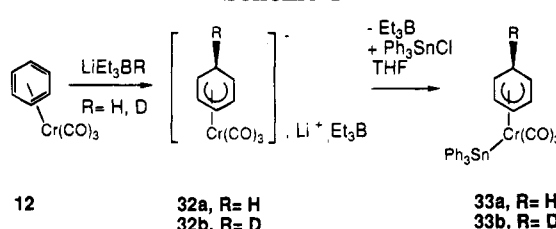
plex **34** (Scheme 3).[29] A 50:50 mixture of complex **12** and neutral tricarbonyl(η^5-cyclohexadienyl)manganese (**35**) is obtained as a result of hydride transfer from complex **32a** to the electrophilic complex **34**.[19]

Treatment of (η^6-benzene)Cr(CO)$_3$ (**12**) with LiEt$_3$BR (R = H, D) in THF gave the lithium salts of the anionic tricarbonyl(η^5-cyclohexadienyl)chromium complexes **32a** (R = H) and **32b** (R = D) (Scheme 4). Trapping the anionic complexes **32a** and **32b** with Ph$_3$SnCl yielded the neutral bimetallic complexes **33a** and **33b**. Selected ^{1}H NMR data of anionic complexes **30** and **32** and those of bimetallic complexes **31** and **33** are reported in Table 4.

^{1}H and ^{13}C NMR data confirm that the nucleophilic addition of hydride or deuteride occurred on the exo side of the complexed arene, for example the H$_{1exo}$ resonance at 1.60 ppm of the deuterated complex **32a** is absent and the C1 resonance at 25.8 ppm is a relatively weak triplet with a $^1J_{C-D}$ coupling constant of 20 Hz.

X-ray Single-Crystal Structure Analysis of 33b. Figures 2 and 3 show ORTEP diagrams of complex **33b** molecular structure with the atom-numbering scheme. Relevant bond lengths and angles are listed in Table 5.

Complex **33b** has the usual η^5-bonded cyclohexadienyl structure described for other complexes that have been published[19,4a,30] (Figure 4). The bimetallic moiety Ph$_3$SnCr(CO)$_3$ is approximately symmetrically oriented with respect to a plane perpendicular to and bissecting the cyclohexadienyl ligand through C4 and C1. The five cyclohexadienyl sp^2 carbons are contained in a mean plane (maximum deviation of 0.023 Å). The interplanar

Table 4. ^{1}H NMR Data of Anionic Complexes 30a and 32a and of Bimetallic Complexes 31a and 33a (Chemical Shifts Expressed in δ (ppm)

	H$_{1exo}$	H$_{1endo}$	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$
30a[a]	2.76	3.59	2.63	4.57	5.63		
32a[a]	2.58[d]	2.85[e]	2.53	4.74	5.43	4.74	2.53
31a[b]	2.80	4.06	3.42	3.88	6.71		
33a[c]	1.60[f]	2.43[g]	2.60[h]	3.72[i]	6.06[j]	3.72	2.60

[a] THF-d_8. [b] C$_6$D$_6$. [c] CDCl$_3$. [d] d, J_{gem} = 11 Hz. [e] dt, J_{gem} = 11 Hz, ^3J = 6 Hz. [f] d, J_{gem} = 13 Hz. [g] dt, J_{gem} = 13 Hz, ^3J = 6 Hz. [h] t, ^3J = 6 Hz. [i] t, ^3J = 5 Hz. [j] t, ^3J = 5 Hz.

(29) A series of anionic tricarbonyl(η^5-cyclohexadienyl)chromium complexes have been prepared and their reactivities studied with various electrophiles; see Reference 4a.

(30) One similar neutral complex, **36**, has been isolated and characterized by X-ray diffraction analysis: Kündig, E. P.; Cunningham, A. F.; Paglia, P.; Simmons, D. P.; Bernardinelli, G. *Helv. Chim. Acta* **1990**, *73*, 386.
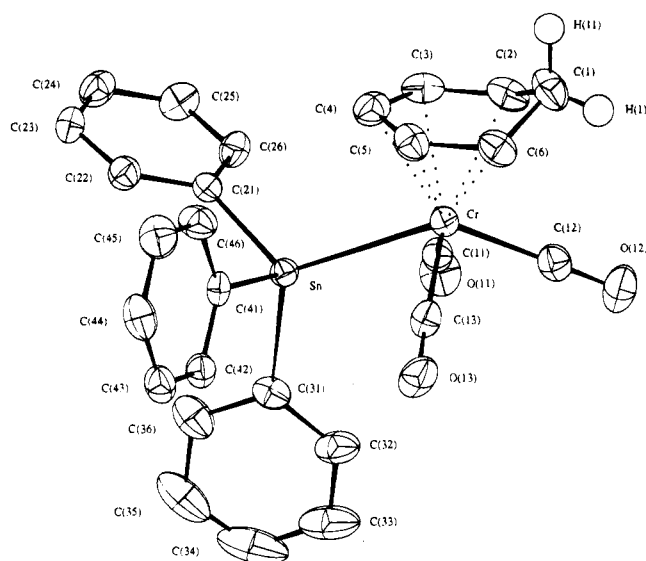
Figure 2. ORTEP diagram of the molecular structure of complex **33b** and the atom numbering.
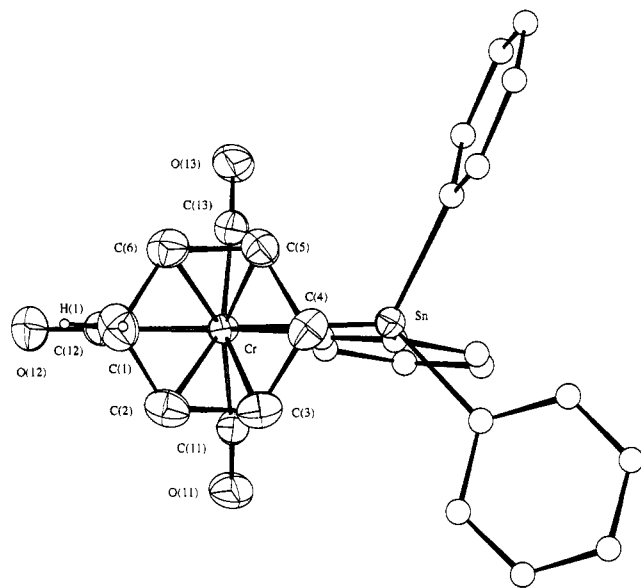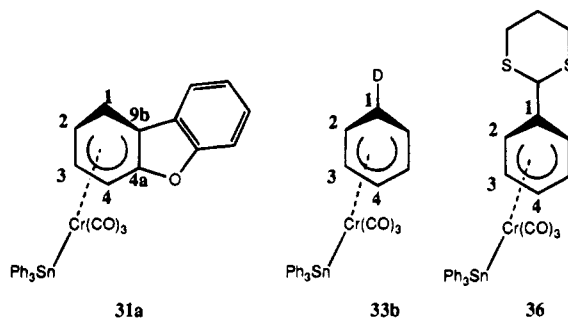

Figure 3. Projection of the cyclohexadienyl ring of **33b** on the plane formed by the three carbonyl oxygen atoms.

Figure 4. Developed formulas of reported substituted neutral $(\eta^5$-cyclohexadienyl)(CO)$_3$Cr$-$Sn(C$_6$H$_5$)$_3$ complexes.

angle between the five cyclohexadienyl carbons and the C1$-$C2$-$C3 plane is 39.2° in the range of values observed for other η^5-cyclohexadienyl complexes but slightly more open than for **31a** (32.5(5)°) and **36**[30] (35.1°). Metal$-$ligand bond lengths can be compared to the two other structures **36** and **31a**[19] described in the literature (Figure 4).

Table 5. Selected Structural Data for Complexes 33b, 36, and 31b

	33b	36[a]	31b
	Bond Distances (Å)		
Cr$-$(C2)	2.276(6)	2.278(10)	2.28(1)
Cr$-$(C3)	2.191(6)	2.187(9)	2.20(1)
Cr$-$(C4)	2.193(6)	2.179(9)	2.18(1)
Cr$-$(C5)	2.187(6)	2.194(10)	
Cr$-$(C6)	2.280(6)	2.304(9)	
Cr$-$Sn	2.713(1)	2.719(2)	2.722(2)
Cr$-$(C4a)			2.249(9)
Cr$-$(C9b)			2.41(1)
Cr$-$CO	1.87	1.85	1.83
(C1)$-$(C2)	1.51(1)	1.507(12)	1.50(2)
(C1)$-$(C9b)			1.50(2)
(C2)$-$(C3)	1.37(1)	1.400(14)	1.38(2)
(C3)$-$(C4)	1.397(9)	1.409(15)	1.46(2)
(C4)$-$(C4a)			1.39(1)
(C4a)$-$(C9b)			1.40(1)
(C1)$-$(C6)	1.51(1)	1.507(14)	
(C4)$-$(C5)	1.407(9)	1.411(13)	
(C5)$-$(C6)	1.370(9)	1.407(15)	
	Bond Angles (deg)		
(C2)$-$(C1)$-$(C6)	102.7(5)	104.0(8)	
(C2)$-$(C1)$-$(C9b)			104.5(9)

[a] See ref 30.

Table 5 shows a comparison of selected data of the three complexes. The average of Cr$-$CO distances in **31a** (1.83 Å) is slightly smaller than in **36** (1.85 Å) and **33b** (1.87 Å). Indeed, the average distance between the Cr atom and C2, C3, C4, and C4a carbons is 2.23 Å and that to C9b is 2.41 Å. This latter longer Cr$-$C9b distance can be attributed to the disubstituted nature of the η^5-cyclohexadienyl ligand in **31a** and reflects the steric strain between the organic and the bimetallic fragments. Indeed, in the case of complexes **36** and **33b**, the average distance between the chromium atom and the five pentadienyl-like carbons is 2.23 Å. The longest and the shortest Cr$-$C distances for **33b** are 2.30 (Cr$-$C6) and 2.18 (Cr$-$C4) Å.

Concluding Remarks

In conclusion, these results show that nucleophilic aromatic substitutions of alkoxy, aryloxy, halogeno, and dimethylamino groups by hydride occur if the corresponding substituted arenetricarbonylchromium complexes are treated with lithium triethylborohydride followed by treatment with acid. Depending on the nature of the substituted arene complex, hydrides can displace these various groups via ipso, cine, and tele nucleophilic aromatic substitution pathways. Usually these reactions are performed by stepwise addition of a hydride and an acid. In some cases, water is acidic enough to protonate the anionic η^5-cyclohexadienyl intermediates. The unprecedented carbon$-$nitrogen and carbon$-$oxygen bond cleavage reactions can be of interest in organic synthesis. The reversibility of the addition of hydrides has been clearly demonstrated in the case of the dibenzofuran complex as well as in the case of a *p*-methoxy-*tert*-butylbenzene complex. The carbon$-$halogen bond cleavage that occurs readily under different conditions is also of interest for the regioselective synthesis of deuterated aromatic compounds and the use of the latter as labeled substrates in biochemistry. Finally, in two cases, the anionic η^5-cyclohexadienyl complexes have been trapped by Ph$_3$SnCl giving rise to bimetallic air-stable complexes. Further study of their reactivity and structural properties is underway and will be the subject of a subsequent article.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. All experiments involving (η^6-arene)tricarbonylchromium complexes were always protected from exposure to light and oxygen. All air-sensitive tricarbonyl(η^5-cyclohexadienyl)-chromium complexes were handled inside a glovebox under a continous flow of dry and purified nitrogen. Solvents used for these very reactive complexes were distilled over sodium—benzophenone ketyl anion and degassed by three freeze—pump—thaw cycles. Tetrahydrofuran (THF) and di-n-butyl ether (DBE) were dried over sodium—benzophenone ketyl anion under dry nitrogen atmosphere and distilled just before use. Deuterated solvents and sample tubes were purged with dry nitrogen to remove oxygen. (η^6-3-Ethylanisole)tricarbonylchromium (**1**), (η^6-anisole)tricarbonylchromium (**11**), complex **16**, tricarbonyl(η^6-diphenyl ether)chromium, tricarbonyl(η^6-2-methylphenyl phenyl ether)chromium (**5**), tricarbonyl(η^6-dibenzofuran)chromium (**18**), tricarbonyl(η^6-4-chlorotoluene)-chromium (**23**), tricarbonyl(η^6-4-fluorotoluene)chromium (**24**), tricarbonyl(η^6-chlorobenzene)chromium, and tricarbonyl(η^6-fluorobenzene)chromium were prepared according to standard procedures. (N,N-Dimethylamino)arenes, giving complexes **25**, **27**, **28**, and **29** after complexation, were obtained from aniline using a direct method of N-dimethylation with trimethyl phosphate.

Products were separated by flash chromatography on silica gel column (15 or 60 μm) under a dry atmosphere nitrogen pressure (1 atm). Diethyl ether and petroleum ether (PE) were used as solvent for elution. Triethylborohydride and triethylborodeuteride THF solutions were purchased from Aldrich Chemical Co.

^{1}H and ^{13}C NMR spectra were acquired on a Brücker AC 200 (resonance frequencies: 200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer and chemical shifts are reported in parts per million (ppm) downfield of Me$_4$Si. All 2D NMR experiments were performed on a Jeol GSX 400 (resonance frequencies: 400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer. ^{1}H NMR spectra were referenced against the residual ^{1}H impurity of the deuterated solvent (δ (ppm) 7.15 (C$_6$D$_6$); 7.24 (CDCl$_3$); 2.05 ((CD$_3$)$_2$CO); 1.73, 3.58 (C$_4$D$_8$O)), and ^{13}C NMR spectra were referenced against the ^{13}C resonance of the solvent (δ 128.0 (C$_6$D$_6$); 77.1 (CDCl$_3$); 29.8, 206.0 ((CD$_3$)$_2$CO); 25.3, 67.4 (C$_4$D$_8$O)). Variable-temperature experiments were performed on a Brucker AC 300 using flame-sealed NMR sample tubes under a 10^{-2} Torr vacuum. Infrared spectra (reported in cm^{-1}) were performed on Perkin-Elmer 1420 and Brücker FT spectrometers. Mass spectra were obtained on a Nermag R 30—40 spectrometer, with a direct insert source, using electronic impact (EI) and chemical ionization (CI) methods. Elemental analyses (reported in percent mass) were performed by Le Service de Microanalyses de l'Université P. et M. Curie and the Service Central d'Analyse du CNRS at Vernaison, France. Melting points were measured on a Reichert apparatus. Crystal structures were determined at the Laboratoire de Chimie des Métaux de Transition, Université P. et M. Curie.

Single-Crystal X-ray Diffraction of Complex 33b. The selected crystal was set up on an Enraf Nonius CAD4F diffractometer. Accurate unit cell dimensions and crystal orientation matrice together with their estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Two standard reflections were monitored periodically; no intensity decay occurred during the data collections. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections were applied (Difabs).[31] Crystallographic data and other pertinent informations are summarized in Table 6.

Structure Solution and Refinement. Computations were performed by using CRYSTALS[32] adapted on a Microvax

(31) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

Table 6. X-ray Diffraction Acqusition and Calculation Data for Complex 33b

empirical formula	C$_{27}$H$_{21}$DCrO$_3$Sn
MW (g·mol^{-1})	566.2
cryst dimens (mm)	0.18 × 0.25 × 0.62
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	8.961(4)
b (Å)	10.853(5)
c (Å)	12.713(2)
α (deg)	85.15(3)
β (deg)	86.26(2)
γ (deg)	72.40(4)
V (Å^3)	1173(15)
Z	2
ϱ (g·cm^{-3})	1.600
T (K)	293
monochromator	graphite
λ(Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	15.45
2θ range (deg)	$3 < 2\theta < 50$
no. of reflectns collected	4310
no. of unique reflectns	4107
merging R factor	0.045
no. of reflections with $I > 3\sigma(I)$	2905
absorption corrected by	Difabs^c
transm coeff	0.89, 1.15
R^a	0.33, $S = 1.55$
$R_w{}^b$	0.037 (unit weight)
no. of variables	289

^{a} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_c)^2]^{1/2}$. ^{c} See ref 31.

II computer. Atomic factor for neutral Cr, Sn, C, O, and H were taken from ref 33. Anomalous dispersion was taken into account. The structure was solved by interpretation of the Patterson maps, which clearly indicated Cr and Sn atom positions. All remaining non-hydrogen atoms were found by successive electron density map calculations. Their atomic coordinates were refined together with anisotropic temperature factors. At this stage, hydrogen atoms were located on a difference electron density map; their coordinates were refined with an overall isotropic temperature factor. Least-squares refinements were carried out by minimizing the function $\sum w(/F_o/ - /F_c/)^2$, where F_o and F_c are the observed and calculated structure factors. The models reached convergence with R and R_w having the values listed in Table 6. The criteria for a satisfactory complete analysis were the ratios of the root-mean-square shift to standard deviation being less than 0.1 and no significant features in the final difference maps.

Atomic coordinates are given in Table 7; selected bond distances and bond angles are given in Table 8. The molecular geometry and the numbering scheme are shown in Figures 2 and 3.

Preparations of (η^6-Arene)tricarbonylchromium Complexes. Tricarbonyl[η^6-2-methoxy(trimethylsilyl)benzene]-chromium (3a). To a solution of complex **11** (732 mg, 3 mmol) in THF (10 mL) was added a hexane solution of n-BuLi (1.5 M, 2 mL, 3 mmol) at -78 °C. The resulting solution was stirred for 30 min, and chlorotrimethylsilane (0.5 mL, 3 mmol) was added dropwise. The solution was warmed and extracted at room temperature with Et$_2$O, washed with water, dried over MgSO$_4$, and filtered through a Celite column, and solvents were removed under reduced pressure to give a yellow residue. Separation of the products by flash chromatography affords the disilylated product (Et$_2$O:PE = 2:98) and the complex **3a** (Et$_2$O:PE = 3:97) which was recrystallized from pentane to give 280 mg (0.88 mmol) in 30% yield, mp 110 °C. MS (CI) (NH$_3$): m/e 334 (M + H + NH$_3$)$^+$, 317 (M + H)$^+$. Anal. Calcd

(32) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *Crystals in Advanced Crystallographic Program System*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1988.

(33) *International Tables for X-ray Crystallography*; Kynoch Press; Birmingham, England, 1974; Vol. IV.

Table 7. Fractional Atomic Coordinates for the Molecular Structure of 33b

atom	x/a	y/b	z/c	$U_{eq}{}^a$
Sn	0.13371(5)	0.20336(4)	0.26635(3)	0.0359
Cr	−0.1298(1)	0.40864(9)	0.26841(7)	0.0379
C(1)	−0.4387(8)	0.5079(8)	0.3534(6)	0.0655
C(2)	−0.3866(8)	0.4177(8)	0.2547(5)	0.0561
C(3)	−0.2939(8)	0.2934(7)	0.2841(5)	0.0535
C(4)	−0.1996(8)	0.2614(6)	0.3716(5)	0.0536
C(5)	−0.1944(7)	0.3623(7)	0.4326(5)	0.0507
C(6)	−0.2890(8)	0.4859(7)	0.4105(5)	0.0574
C(11)	−0.0809(7)	0.3726(6)	0.1273(5)	0.0453
O(11)	−0.0634(6)	0.3581(5)	0.0392(3)	0.0625
C(12)	−0.2028(7)	0.5810(7)	0.2132(5)	0.0506
O(12)	−0.2445(6)	0.6842(5)	0.1788(4)	0.0719
C(13)	0.0360(8)	0.4599(6)	0.3113(5)	0.0483
O(13)	0.1304(6)	0.4971(4)	0.3414(4)	0.0609
C(21)	0.0992(6)	0.0226(5)	0.2364(4)	0.0389
C(22)	0.1793(7)	−0.0904(6)	0.2936(5)	0.0491
C(23)	0.1711(8)	−0.2104(6)	0.2697(5)	0.0509
C(24)	0.0826(8)	−0.2209(6)	0.1889(5)	0.0522
C(25)	0.0016(8)	−0.1108(6)	0.1319(5)	0.0518
C(26)	0.0076(7)	0.0106(6)	0.1556(5)	0.0461
C(31)	0.3153(7)	0.2258(6)	0.1530(4)	0.0455
C(32)	0.3108(9)	0.3413(8)	0.0995(5)	0.0607
C(33)	0.424(1)	0.355(1)	0.0271(7)	0.0801
C(34)	0.547(1)	0.250(2)	0.0074(7)	0.0878
C(35)	0.560(1)	0.132(1)	0.0575(8)	0.0871
C(36)	0.4399(9)	0.1189(8)	0.1327(6)	0.0693
C(41)	0.2432(6)	0.1682(5)	0.4163(4)	0.0361
C(42)	0.3828(7)	0.1976(6)	0.4241(5)	0.0440
C(43)	0.4547(7)	0.1797(6)	0.5195(5)	0.0521
C(44)	0.3879(8)	0.1358(7)	0.6091(5)	0.0566
C(45)	0.2502(8)	0.1072(7)	0.6057(5)	0.0597
C(46)	0.1763(8)	0.1238(7)	0.5083(5)	0.0550

^{a} $U_{eq} = (U_1U_2U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the $\mathbf{U}_{ij}$ matrix.

for $C_{13}H_{16}CrO_4Si$: C, 49.37; H, 5.15. Found: C, 49.67; H, 5.06. IR (neat): ν(C=O) 1954, 1878 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.67 (td, H$_4$, ^3J = 6.5 Hz, ^4J = 1.5 Hz), 5.58 (dd, H$_6$, ^3J = 6.5 Hz, ^4J = 1.5 Hz), 4.97 (d, H$_3$, ^3J = 6.5 Hz), 4.77 (t, H$_5$, ^3J = 6.5 Hz), 3.67 (s, CH$_3$O), 1.25 (s, (CH$_3$)$_3$Si). ^{13}C NMR (CDCl$_3$): δ 0.3 (CH$_3$Si), 55.5 (CH$_3$O), 73.6−88.1−96.0−101.0 (C$_{3,4,5,6}$), 108.0 (C$_2$), 123.2 (C$_1$), 233.1 (CO).

Tricarbonyl[η⁶-2-phenoxy(trimethylsilyl)benzene]chromium (3b): phenoxybenzenetricarbonylchromium (3.06 g, 10 mmol), THF (25 mL), n-BuLi (1.6 M, 6.25 mL), T = −78 °C, ClSi(CH$_3$)$_3$ (1.3 mL, 10 mmol); stirring 30 min. Complex **3b** (2.1 g, 5.5 mmol, 55% yield), mp 107 °C. MS (CI) (NH$_3$): m/e 379 (M + H)$^+$, 351 (M + H − CO)$^+$, 243 (M + H − Cr(CO)$_3$)$^+$. Anal. Calcd for C$_{18}$H$_{12}$CrO$_4$Si: C, 57.14; H, 4.82. Found: C, 57.06; H, 4.76. IR (neat): ν(C=O) 1962, 1878 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.28 (m, 5H, OPh), 5.64 (d, H$_6$, ^3J = 5.0 Hz), 5.55 (t, H$_4$, ^3J = 7.0 Hz), 4.68 (m, H$_{5,3}$), 0.39 (s, (CH$_3$)$_3$Si).

Tricarbonyl(η⁶-2-*tert*-butylanisole)chromium (7a): 2-*tert*-butylanisole (3.3 g, 20 mmol), Cr(CO)$_6$ (4.6 g, 20 mmol), THF (10 mL), and DBE (90 mL); reflux 5 days. Complex **7a** (45% yield, 2.5 g), mp 140 °C. Anal. Calcd for C$_{14}$H$_{16}$CrO$_4$: C, 56.00; H, 5.37. Found: C, 55.87; H, 5.35. IR (CH$_2$Cl$_2$): ν-(C=O) 1960, 1875 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.78 (d, H$_3$, ^3J = 7 Hz), 5.59 (t, H$_5$, ^3J = 7 Hz), 5.00 (d, H$_6$, ^3J = 7 Hz), 4.73 (t, H$_4$, ^3J = 7 Hz), 3.79 (s, MeO), 1.35 (s, (CH$_3$)$_3$C). ^{13}C NMR (CDCl$_3$): δ 30.8 (CH$_3$-C), 34.8 (CH$_3$-C), 55.4 (CH$_3$-O), 73.9−96.8 (C$_{3,4,5,6}$), 110.7 (C$_2$), 143.4 (C$_1$), 234.0 (CO). For **7b, 7c, 9, 13**, and **16**, see supplementary material except for NMR. For **7b**. ^{1}H NMR (CDCl$_3$): δ 5.51 (t, H$_5$, ^3J = 6.6 Hz), 5.25 (s, H$_2$, ^3J = 6.6 Hz), 5.08 (d, H$_4$, ^3J = 6.6 Hz), 4.98 (d, H$_6$, ^2J = 6.6 Hz), 3.71 (s, MeO), 1.32 (s, (CH$_3$)$_3$C). ^{13}C NMR (CDCl$_3$): δ 30.9 (CH$_3$-C), 34.4 (CH$_3$-C), 55.7 (CH$_3$O), 76.7−93.8 (C$_{2,4,5,6}$), 126.4 (C$_3$), 143.3 (C$_1$), 233.8 (CO). For **7c**. ^{1}H NMR (CDCl$_3$): δ 5.66 (d, H$_{3,5}$, ^3J = 7.2 Hz), 5.02 (d, H$_{2,6}$, ^3J = 7.2 Hz), 3.70 (s, MeO), 1.24 (s, (CH$_3$)$_3$C). ^{13}C NMR (CDCl$_3$): δ 30.7 (CH$_3$C), 34.8 (CH$_3$C), 55.4 (CH$_3$O), 76.6 (C$_{3,5}$), 93.8 (C$_{2,6}$), 116.2 (C$_4$), 143.4 (C$_1$), 233.8 (CO). For **9**. ^{1}H NMR ((CD$_3$)$_2$CO): δ 5.27 (s, 3H,

Table 8. Selected Bond Distances (Å) and Bond Angles (deg) for Cr(C₆H₇)(CO)₃−Sn(C₆H₅)₃

Bond Distances			
Cr−Sn	2.713(1)		
		C(1)−C(2)	1.51(1)
Cr−C(2)	2.276(6)	C(2)−C(3)	1.37(1)
Cr−C(3)	2.191(6)	C(3)−C(4)	1.397(9)
Cr−C(4)	2.193(6)	C(4)−C(5)	1.407(9)
Cr−C(5)	2.187(6)	C(5)−C(6)	1.370(9)
Cr−C(6)	2.280(6)	C(6)−C(1)	1.51(1)
Cr−C(11)	1.864(6)	C(11)−O(11)	1.138(7)
Cr−C(12)	1.875(7)	C(12)−O(12)	1.128(7)
Cr−C(13)	1.863(7)	C(13)−O(13)	1.141(7)
Sn−C(21)	2.145(6)	Sn−C(31)	2.158(6)
Sn−C(41)	2.153(5)		

Bond Angles			
C(1)−C(2)−C(3)	120.5(6)	C(4)−C(5)−C(6)	120.2(6)
C(2)−C(3)−C(4)	119.9(6)	C(5)−C(6)−C(1)	119.9(6)
C(3)−C(4)−C(5)	118.0(6)	C(6)−C(1)−C(2)	102.7(5)
Cr−C(11)−O(11)	174.0(6)	C(11)−Cr−C(12)	84.1(3)
Cr−C(12)−O(12)	178.8(6)	C(11)−Cr−C(13)	105.1(3)
Cr−C(13)−O(13)	175.5(6)	C(12)−Cr−C(13)	83.8(3)
C(2)−Cr−C(11)	95.7(3)	C(5)−Cr−C(11)	154.0(3)
C(2)−Cr−C(12)	83.3(3)	C(5)−Cr−C(12)	118.5(3)
C(2)−Cr−C(13)	154.1(3)	C(5)−Cr−C(13)	91.0(3)
C(3)−Cr−C(11)	92.0(3)	C(6)−Cr−C(11)	156.0(3)
C(3)−Cr−C(12)	118.2(3)	C(6)−Cr−C(12)	83.5(3)
C(3)−Cr−C(13)	153.8(3)	C(6)−Cr−C(13)	93.8(3)
C(4)−Cr−C(12)	142.5(3)		
C(4)−Cr−C(11)	116.6(2)		
C(4)−Cr−C(13)	116.7(3)		
Sn−Cr−C(2)	130.7(2)	Sn−Cr−C(3)	95.7(2)
Sn−Cr−C(4)	77.5(2)	Sn−Cr−C(5)	93.3(2)
Sn−Cr−C(6)	127.7(2)		
Sn−Cr−C(11)	73.5(2)	Sn−Cr−C(12)	140.0(2)
Sn−Cr−C(11)	73.5(2)		
Cr−Sn−C(21)	115.2(1)	C(21)−Sn−C(31)	105.0(2)
Cr−Sn−C(31)	114.9(2)	C(21)−Sn−C(41)	105.0(2)
Cr−Sn−C(41)	111.3(1)	C(31)−Sn−C(41)	104.5(2)

H-Ar), 3.83 (s, 9H, OCH$_3$). ^{13}C NMR ((CD$_3$)$_2$CO): δ 56.5-(OCH$_3$), 66.3(C$_{2,4,6}$), 144.6(C$_{1,3,5}$), 233.0(CO). For **13**.[34] ^{1}H NMR ((CD$_3$)$_2$CO): δ 5.72 (t, H$_5$, J = 6.5 Hz), 5.20 (d, H$_{4,6}$, J = 6.5 Hz), 3.86 (s, 6H, OCH$_3$), 3.82 (s, 3H, OCH$_3$). ^{13}C NMR ((CD$_3$)$_2$-CO): δ 56.9 (OCH$_3$), 65.7 (OCH$_3$), 71.5 (C$_{4,6}$), 91.6 (C$_5$), 141.6 (C$_{1,2,3}$), 235.3 (CO). For **16**. ^{1}H NMR (CDCl$_3$): δ 5.43 (dd, H$_{5,8}$, ^3J = 5.0 Hz, ^4J = 3.0 Hz), 5.02 (dd, H$_{6,7}$, ^3J = 5.0 Hz, ^4J = 3.0 Hz), 4.24 (s, CH$_2$CH$_2$). ^{13}C NMR (CDCl$_3$): δ 64.8 (C$_{2,3}$), 83.5−87.8 (C$_{5,8,6,7}$), 126.4 (C$_{4',1'}$), 233.8 (CO).

Tricarbonyl[η⁶-2-fluoro(triisopropylsilyl)benzene]chromium (20): THF (15 mL), tricarbonyl(η⁶-fluorobenzene)-chromium (1.16 g, 5 mmol), n-BuLi (1.6 M, 3.13 mL, 5 mmol), −78 °C. The resulting solution was stirred for 30 min and ClSi(i-Pr)$_3$ (0.70 mL, 5.5 mmol) was added. The resulting mixture was extracted with Et$_2$O, washed with water and brine, filtered through a Celite column, and dried over MgSO$_4$; solvents were removed under reduced pressure. The crude product was purified by flash chromatography on silica gel to give **20** (1.03 g, 2.7 mmol, 54% yield), mp 105°C (dec). Anal. Calcd for C$_{18}$H$_{25}$CrFO$_3$Si: C, 55.67; H, 6.44. Found: C, 55.48; H, 6.54. IR(neat): ν(C=O) 1970, 1892 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.66 (m,H$_4$), 5.52 (m, H$_6$), 5.21 (t, H$_5$, ^3J = 6 Hz), 4.78 (m, H$_3$), 1.78 (sept, CHCH$_3$, ^3J = 7 Hz), 1.17 (d, CHCH$_3$, ^3J = 7 Hz). For complex **22**, see supplementary material except for NMR data. For **22**. ^{1}H NMR (CDCl$_3$): δ 5.59 (t, H$_4$, ^3J = 6.5 Hz), 5.52 (dd, H$_6$, ^3J = 6.5 Hz), 5.32 (d, H$_3$, ^3J = 6.5 Hz), 4.89 (t, H$_5$, ^3J = 6.5 Hz), 0.41 (Si(CH$_3$)$_3$).

Tricarbonyl [η⁶-2-(N,N-dimethylamino)(trimethylsilyl)benzene]chromium (29a) and Tricarbonyl[η⁶-3-(N,N-dimethylamino)(trimethylsilyl)benzene]chromium (29b). To a THF solution (10 mL) of 2,2,6,6-tetramethylpiperidine (678 mg, 0.81 mL, 4.8 mmol) was added dropwise a solution

(34) Saillard, J. Y.; Grandjean, D.; Le Maux, P.; Jaouen, G. *New J. Chem.* **1981**, *5*, 153.

of n-BuLi (1.6 M, 3.0 mL, 4.8 mmol) in hexane, at -78 °C. The resulting solution was stirred for 10 min, and a solution of (η^6-N,N-dimethylaniline)Cr(CO)$_3$ (1.01 g, 4. mmol) in THF (10 mL) was added. The solution was stirred again for 30 min at -78 °C, and Me$_3$SiCl (1.3 g, 1.53 mL, 12 mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and extracted with Et$_2$O. The organic phase was washed with water and brine, dried over MgSO$_4$, and filtered through a Celite column; solvents were removed under reduced pressure. The yellow residue was purified by flash chromatography on silica gel to give the starting complex, (η^6-N,N-dimethylaniline)Cr(CO)$_3$, (PE 100%), complex **29a** (Et$_2$O:PE = 10:90), and complex **29b** (Et$_2$O:PE = 20:80). After recrystallization in pentane, complexes **29a** (200 mg, 0.61 mmol, 15% yield) and **29b** (739 mg, 2.25 mmol, 57% yield) were obtained as pure yellow crystals. For complex **29a**, mp 78 °C. Anal. Calcd for C$_{14}$H$_{19}$CrNO$_3$Si: C, 51.05; H, 5.81; N, 4.25. Found: C, 51.31; H, 5.85; N, 4.28. MS (CI) (NH$_3$): m/e 330 (M + H)$^+$, 302(M + H $-$ CO)$^+$, 194(M + H $-$ Cr(CO)$_3$)$^+$. IR (neat): ν-(CO) 1956, 1872 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.60 (td, H$_4$, ^3J = 6.5 Hz, ^4J = 1.5 Hz), 5.49 (dd, H$_6$, ^3J = 6.0 Hz, ^4J = 1.5 Hz), 4.96 (t, H$_5$, ^3J = 6.0 Hz), 4.94 (d, H$_3$, ^3J = 6.5 Hz), 2.63 (s, 6H, CH$_3$N), 0.36 (s, 9H, CH$_3$Si). ^{13}C NMR (CDCl$_3$): δ 0.7 (CH$_3$Si), 45.6 (CH$_3$N), 79.9$-$88.4$-$95.2$-$101.5 (C$_{3,4,5,6}$), 98.9 (C$_1$), 141.0 (C$_2$), 233.8 (CO). For complex **29b**, mp 97 °C. Anal. Calcd for C$_{14}$H$_{19}$CrNO$_3$Si: C, 51.05; H, 5.81; N, 4.25. Found: C, 51.13; H, 5.78; N, 4.14. MS (CI) (NH$_3$): m/e 330 (M + H)$^+$, 302 (M + H $-$ CO)$^+$, 194 (M + H $-$ Cr(CO)$_3$)$^+$. IR(neat): ν-(CO) 1944, 1852 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.55 (t, H$_5$, ^3J = 6.5 Hz), 4.95 (dd, H$_6$, ^3J = 6.5 Hz, ^4J = 2 Hz), 4.81 (d, H$_4$, ^3J = 6.0 Hz), 4.72 (s, H$_2$), 2.87 (s, 6H, CH$_3$N), 0.30 (s, 9H, CH$_3$-Si). ^{13}C NMR (CDCl$_3$): δ 0.6 (CH$_3$Si), 41.0 (CH$_3$N), 76.5 (C$_2$), 79.5 (C$_6$), 89.3 (C$_4$), 97.5 (C$_5$), 99.3 (C$_1$), 135.5 (C$_3$), 233.2 (CO). ^{13}C NMR signals were assigned according to a ^{13}C$-$^{1}H correlation 2D NMR experiment.

Reaction of Lithium Triethylborohydride with (η^6-Alkoxyarene)Cr(CO)$_3$ and [η^6-(Aryloxy)arene]Cr(CO)$_3$ Complexes. *Ipso* Aromatic Nucleophilic Substitutions. Tricarbonyl(η^6-ethylbenzene)chromium (2a): **1** (272 mg, 1 mmol), THF (15 mL), LiEt$_3$BH (1 M, 2 mL, 2 mmol). The resulting solution was refluxed for 2 h and treated with a diluted solution of chlorhydric acid or trifluoroacetic acid. The mixture was extracted with Et$_2$O, washed with a saturated solution of Na$_2$CO$_3$ and with brine, dried over Na$_2$SO$_4$, and filtered through a Celite column. Solvents were removed under reduced pressure. The yellow residue was recrystallized in a mixture of hexane and acetone to give pure yellow crystals of complex **2a** (241 mg, 0.995 mmol, 100% yield). Spectrometric and analytical data were in agreement with a standard sample. For **2b**, see supplementary material.

Tricarbonyl(η^6-*tert*-butylbenzene)chromium (8): 7c (150 mg, 0.5 mmol), THF (20 mL), LiEt$_3$BH (1 M, 2 mL, 2 mmol), reflux 24 h; hydrolysis. For complex **8** (110 mg, 0.4 mmol, 80%, yield). ^{1}H NMR (CDCl$_3$): δ 5.52 (d, H$_{2,6}$, ^3J = 7 Hz), 5.38 (t, H$_4$, ^3J = 7 Hz), 5.22 (t, H$_{3,5}$, ^3J = 7 Hz), 1.28 (s, (CH$_3$)$_3$C). ^{13}C NMR (CDCl$_3$): δ 31.1 (CH$_3$C), 34.1 (CH$_3$C), 90.8 (C$_{2,6}$), 92.2 (C$_4$), 92.6 (C$_{3,5}$), 126.4 (C$_1$), 233.6 (CO). For **8-*p***, **8-*m***, and **8-*o***, see supplementary material.

Tricarbonyl(η^6-benzene)chromium (12a): **9** (471 mg, 1.5 mmol), THF (10 mL), LiAlH$_4$ (118 mg, 3.1 mmol) in THF (5 mL), reflux 24 h; hydrolysis. For complex **12a** data (320 mg, 1.5 mmol, 100% yield, see supplementary material.

Tricarbonyl(η^6-1,3-dimethoxybenzene)chromium (10a): **9** (155.2 mg, 0.51 mmol), THF (20 mL), LiEt$_3$BH (1 M, 2.2 mL, 2.2 mmol), stirring 20 min, room temperature. The composition of the residue was obtained by ^{1}H NMR spectroscopy and based on comparison with ^{1}H NMR spectra from reference samples. According to ^{1}H NMR spectra, the composition (molality) was as follows: **10a**, 73%; **11**, 13%; starting complex, 14%. For **10b**, see supplementary material.

(η^6-Anisole)tricarbonylchromium (11): **13** (155.2 mg, 0.51 mmol), THF (15 mL), LiEt$_3$BH (1M, 0.8 mL, 0.8 mmol),

CF$_3$CO$_2$H (0.5 mL). The composition of the residue was obtained by ^{1}H NMR spectroscopy and based on comparison with ^{1}H NMR spectra of reference samples. According to ^{1}H NMR spectra, the composition (molality) was as follows: **11**, 36%; (η^6-1,2-dimethoxybenzene)Cr(CO)$_3$, 30%; **12**, 5%; starting complex **13**, 29%.

2-[Tricarbonyl(η^6-phenoxy)chromium]ethanol (17a): **16** (272 mg, 1 mmol), THF (30 mL), HMPA (0.2 ml), LiEt$_3$BH (1 M, 1.5 mL, 1.5 mmol), reflux 23 h; hydrolysis. The yellow residue was chromatographed on silica gel to give the starting complex **16** and **12** (Et$_2$O:PE = 50:50, 10% (molality) of **12** and **17a** (100% Et$_2$O). **17a** was recrystallized in a mixture of pentane and Et$_2$O and was obtained pure (91 mg as yellow needles, 0.33 mmol, 33% yield). Anal. Calcd for C$_{11}$H$_9$CrO$_5$: C, 48.17; H, 3.65. Found: C, 47.91; H, 3.67. MS (CI) (NH$_3$): m/e 292 (M + H + NH$_3$)$^+$, 275 (M + H)$^+$, 139 (M + H $-$ Cr-(CO)$_3$)$^+$. IR (Nujol): ν(C=O) 1975, 1900 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.54 (t, H$_{3,5}$, ^3J = 6.0 Hz), 5.13 (d, H$_{2,6}$, ^3J = 6.0 Hz), 4.88 (t, H$_4$, ^3J = 6.0 Hz), 3.96 (m, CH$_2$CH$_2$), 1.60 (s, OH). ^{13}C NMR (CDCl$_3$): δ 61.0 (CH$_2$OAr), 70.1 (CH$_2$OH), 78.7 (C$_{2,6}$), 85.6 (C$_4$), 95.0 (C$_{3,5}$), 120.0 (C$_1$), 233.1 (CO). ^{13}C NMR signals were assigned according to a ^{13}C$-$^{1}H correlation 2D NMR experiment.

2-[Tricarbonyl(η^6-2'-deuteriophenoxy)chromium]ethanol (17b): **16** (272 mg, 1 mmol), THF (30 mL), LiEt$_3$BD (1M, 1.5 mL, 1.5 mmol), complex **17b** (60 mg, 0.22 mmol, 22% yield), mp 94 °C. MS (CI) (NH$_3$): m/e 293 (M + H + NH$_3$)$^+$, 276 (M + H)$^+$, 140 (M + H $-$ Cr(CO)$_3$)$^+$. ^{13}C NMR (CDCl$_3$): δ 61.0 (CH$_2$OAr), 70.1 (CH$_2$OH), 78.5 (t, C$_2$, $^1J_{C-D}$ = 27.0 Hz), 78.8 (C$_6$), 85.6 (C$_4$), 95.0 (C$_{3,5}$), 120.0 (C$_1$), 233.1 (CO).

2-[Tricarbonyl(η^6-phenyl)chromium]phenol (19): **18** (1g, 3.28 mmol), THF (100 mL), LiEt$_3$BH (1 M, 6.56 mL, 6.56 mmol), reflux 48 h; HCl treatment. Complex **19** (753 mg, 2.46 mmol, 75% yield). Anal. Calcd for C$_{15}$H$_{10}$CrO$_4$: C, 58.82; H, 3.26. Found: C, 58.68; H, 3.31. MS (CI) (NH$_3$): m/e 324 (M + H + NH$_3$)$^+$, 307 (M + H)$^+$, 171 (M + H $-$ Cr(CO)$_3$)$^+$. IR (CHCl$_3$): ν(O$-$H) 3560, ν(C=O) 1975, 1980, 1905 cm^{-1}. ^{1}H NMR ((CD$_3$)$_2$CO): δ 8.35 (s, OH), 6.96 (m, 4H, HAr), 6.06 (m, H$_{3,5}$, ArCr), 5.70 (m, H$_{2,4,6}$, ArCr). ^{13}C NMR (CDCl$_3$): δ 92.1$-$92.3$-$95.0 (C$_{2,6,3,5,4}$, ArCr), 106.5 (C$_1$, ArCr), 116.9 (C$_6$, Ar), 121.3 (C$_4$, Ar), 130.5 (C$_{3,5}$, Ar), 132.0 (C$_2$, Ar), 152.5 (C$_1$, Ar), 233.0 (CO).

^{1}H NMR Study of Deuteride Addition to Tricarbonyl-(η^6-3-ethylanisole)chromium. To a solution of LiEt$_3$BD (0.11 mmol, 0.11 mol·dm^{-3}) in THF-d_8 (1 mL) was added the complex **1** (16 mg, 5.88 × 10^{-2} mmol, 0.0588 mol·dm^{-3}). The solution was stirred for 1 min. A small quantity of the previous solution (0.5 mL) was injected into a NMR sample tube via a syringe. The resulting solution was frozen at -180 °C under N$_2$ and the sample tube was sealed under vacuum. ^{1}H NMR experiments were carried out at room temperature and at 80 °C. For Et$_3$BDLi. ^{1}H NMR (C$_4$D$_8$O): δ 0.63 (m, BCH$_2$CH$_3$), -0.14 (m, BCH$_2$CH$_3$). As the reaction proceeded, the amount of complex **1** decreased. A major new compound, (η^6-3-deuterioethylbenzene)Cr(CO)$_3$ (**2b**), was detected after several hours of reaction in the NMR probe along with uncharacterized products.

^{1}H NMR Study of Hydride Addition to Complex 9. To a solution of complex **9** (10 mg, 0.033 mmol) in THF-d_8 (2 mL) was aded a solution of LiEt$_3$BH (1 M, 6.6 μL, 0.066 mmol) in THF-d_8. The solution of LiEt$_3$BH in THF-d_8 was obtained from the commercial solution by removing THF under vacuum and adding the same volume of deuterated solvent. The dark red solution was stirred for 1 min and quickly cooled at -40 °C. A small quantity of the previous solution (0.25 mL) was injected under N$_2$ in a NMR sample tube via a syringe and diluted with THF-d_8 (0.75 mL). The resulting dark red solution was frozen and the sample tube was sealed under dry N$_2$. All NMR experiments were carried out at room temperature. For complex **9**. ^{1}H NMR (C$_4$D$_8$O): δ 5.23 (s, H$_{2,4,6}$), 3.78 (s, CH$_3$O). For complex **10**. ^{1}H NMR (C$_4$D$_8$O): δ 5.78 (t, H$_5$, ^3J = 6.7 Hz),

5.44 (d, H_2, ^4J = 2 Hz), 5.07 (dd, $H_{4,6}$, ^3J = 6.7 Hz, ^4J = 2 Hz), 3.75 (s, CH_3O).

Cine and Tele−Meta Aromatic Nucleophilic Substitutions. Tricarbonyl($η^6$-toluene)chromium (6). To a solution of **5** (320 mg, 1 mmol) in THF (40 mL) was added a solution of $LiEt_3BH$ (1 M, 4 mL, 4 mmol) in THF. The resulting solution was refluxed for 48 h and added to a solution of CF_3CO_2H (8 mL) in THF (7 mL). The solution was neutralized with a concentrated aqueous solution of NaOH and extracted with Et_2O. The organic phase was washed with water and brine, dried over $MgSO_4$, and filtered through a Celite column; solvents were removed under reduced pressure. The crude product was recrystallized in a mixture of pentane and Et_2O to give 78 mg of pure complex **6** (0.55 mmol, 55% yield). Spectrometric and analytical data were in agreement with those published in the literature.[21] IR (neat): $ν(C=O)$ 1982, 1868 cm^{-1}. ^1H NMR (CDCl$_3$): $δ$ 5.40 (t, $H_{3,5}$, ^3J = 6.0 Hz), 5.14 (m, $H_{2,4,6}$, ^3J = 6.0 Hz), 2.16 (s, CH_3). ^{13}C NMR (C_6D_6): $δ$ 20.2 (CH_3), 89.3 (C_4), 92.5 ($C_{2,6}$), 94.0 ($C_{3,5}$), 109.8 (C_1), 233.8 (CO). ^{13}C NMR signals were assigned according to ^{13}C−^1H correlation 2D NMR and selective heteronuclear irradiation experiments. For **6-o**, see supplementary material.

Tricarbonyl[$η^6$-(trimethylsilyl)benzene]chromium (4): **3b** (189 mg, 0.5 mmol), THF (15 mL), $LiEt_3BH$ (1 M, 2 mL, 2 mmol), refluxed 24 h, CF_3CO_2H (2 mL), THF (4 mL). Complex **4** (101 mg, 0.35 mmol, 71% yield), mp 99 °C. MS (CI) (NH$_3$): m/e 287 (M + H)$^+$, 259 (M + H − CO)$^+$, 153 (M + H − Cr(CO)$_3$)$^+$. IR (neat): $ν(C=O)$ 1944, 1864 cm^{-1}. ^1H NMR data were in agreement with a standard sample. For **4-p**, see supplementary material.

Kinetic Study of Hydride Addition to Tricarbonyl($η^6$-*p-tert*-butylanisole)chromium (7c). To a solution of **7c** in THF was added a solution of $LiEt_3BD$ in THF at 20 °C. Aliquots of the reaction medium were removed every 30 min for 1 h and every hour for 7 h. Two aliquots were removed after 26 and 33 h of reaction. All samples were injected in THF solutions of trifluoroacetic acid in excess. Resulting mixtures were extracted with diethyl ether and washed with a diluted solution of NaOH and with brine. Organic phases were dried over $MgSO_4$ and filtered through Celite. Solvents were removed under reduced pressure to afford crude solvent-free oily residues that were weighed and analyzed by ^1H NMR.

Reaction of Lithium Triethylborohydride with Tricarbonyl($η^6$-halogenoarene)Chromium Complexes. Hydrodechlorination. Tricarbonyl($η^6$-monodeuteriotoluene)chromium (6-m, 6-o): **23** (262.5 mg, 1 mmol), THF (10 mL), LiAlD$_4$ (155.9 mg, 3.7 mmol), THF (5 mL), room temperature, stirring 5 h, CF_3CO_2H (2 mL), THF (5 mL); **6-m** and **6-o** (228 mg, 0.995 mmol, 100% yield). The composition of the mixture was obtained by analysis of ^1H NMR signal intregration values (I) of $H_{3,5}$ and $H_{2,4,6}$ and according to ^{13}C NMR spectra for the position of deuterium on the aromatic ring. Values were as follows: I = 5.5 ($H_{3,5}$), I = 10.6 ($H_{2,4,6}$). Consequently, the composition (molality) was 0.66 **6-m** and 0.34 **6-o**.

Tricarbonyl($η^6$-3-deuteriotoluene)chromium (6-m): **23** (262.5 mg, 1 mmol), THF (20 mL), $LiEt_3BD$ (1 M, 4.5 mL, 4.5 mmol), room temperature, stirring for 1 day.

An initial amount (10 mL) was added dropwise to a solution of CF_3CO_2H (1 mL) in THF (5 mL) under N_2 atmosphere. The resulting red solution turns to yellow after a few seconds. This solution was then extracted with Et_2O, washed twice with a concentrated aqueous NaOH solution and with brine, dried over $MgSO_4$, and filtered through a Celite column; solvents were removed under reduced pressure. The crude product was recrystallized in PE and the pure isomer **6-m** was obtained (114 mg, 0.497 mmol, 100% yield). ^1H NMR (C_6D_6): $δ$ 4.47 (t, H_5, ^3J = 6 Hz), 4.19 (s + d, $H_{2,4,6}$, ^3J = 6 Hz), 1.50 (CH_3).

The second part of the initial reaction medium was treated similarly with CF_3CO_2D (99.5% D, 1 mL), in THF (5 mL). After extraction and purification the complex **6-o**, **-m** deuterated at the 2 and 3 positions was obtained, 98% yield (113 mg, 0.49

mmol). ^1H NMR (C_6D_6): $δ$ 4.47 (t + d, H_5, 1H, ^3J = 6 Hz), 4.19 (m, $H_{2,4,6}$, 2H, ^3J = 6 Hz), 1.50 (CH_3).

Tricarbonyl[$η^6$-4-deuterio(trimethylsilyl)benzene]chromium (4-p): **22** (160 mg, 0.5 mmol), THF (7.5 mL), $LiEt_3BD$ (1 M, 2.5 mL, 2.5 mmol), stirring 50 min at −78 °C, CF_3CO_2H (2 mL), THF (3 mL); complex **4-p** (143 mg, 0.5 mmol, 100% yield). Spectroscopic and analytical data were in agreement with those obtained previously.

Hydrodefluorination. Tricarbonyl($η^6$-toluene)chromium (6): **24** (246 mg, 1 mmol), THF (20 mL), $LiEt_3BH$ (1 M, 2.2 mL, 2.2 mmol); complex **6** (161 mg, 0.70 mmol, 70% yield). Spectrometric and analytical data were in agreement with a standard sample.

Tricarbonyl($η^6$-4-deuteriotoluene)chromium (6-p): **24** (246 mg, 1 mmol), THF (20 mL), $LiEt_3BD$ (1 M, 2 mL, 2 mmol), stirring 20 h, hydrolysis; complex **6-p** (163 mg, 0.71 mmol, 71% yield).

Tricarbonyl($η^6$-2-deuteriotoluene)chromium (6-o): ($η^6$-2-Fluorotoluene)Cr(CO)$_3$ (123 mg, 0.5 mmol), THF (15 mL), $LiEt_3BD$ (1 M, 2 mL, 2 mmol) in THF, stirring 20 h; hydrolysis; complex **6-o** was obtained (80 mg, 0.35 mmol, 70% yield).

Tricarbonyl[$η^6$-4-deuterio(triisopropylsilyl)benzene]chromium (21-p), Treatment with CF_3CO_2H−THF: **20** (194 mg, 0.5 mmol), THF (7.5 mL), $LiEt_3BD$ (1 M, 2.5 mL, 2.5 mmol), stirring 3 h at 20 °C, CF_3CO_2H (2 mL), THF (3 mL); complex **21-p** (160 mg, 0.43 mmol, 86% yield). ^1H NMR (CDCl$_3$): $δ$ 5.49 (d, $H_{2,6}$, 2H, ^3J = 6.5 Hz), 5.14 (d, $H_{3,5}$, 2H, ^3J = 6.5 Hz), 1.30 (sept, C*H*CH$_3$, 3H), 1.15 (d, CHC*H*$_3$, 18H, ^3J = 6.5 Hz).

Tricarbonyl[$η^6$-4-deuterio(triisopropylsilyl)benzene]chromium (21-p), Treatment with Water: **20** (194 mg, 0.5 mmol), THF (7.5 mL), $LiEt_3BD$ (1 M, 2.5 mL, 2.5 mmol), stirring 3 h at 20 °C, hydrolysis; complex **21-p** (112 mg, 0.3 mmol, 60% yield). The same results were obtained when the initial solution of **20** and $LiEt_3BD$ was stirred for 50 min at −78 °C before acid treatment.

Reaction of Lithium Triethylborohydride with [$η^6$-(N,N-Dimethylamino)arene]tricarbonylchromium Complexes. Tricarbonyl[$η^6$-4-deuterio-(N,N-dimethylamino)benzene]chromium (26b). To a solution of **25** (287 mg, 1 mmol) in THF (40 mL) was added a solution of $LiEt_3BD$ (1 M, 4 mL, 4 mmol) in THF. The resulting mixture was refluxed for 18 h and treated with a diluted hydrochloric aqueous solution. The mixture was extracted with Et_2O, and the organic phase was washed with water and brine, dried over $MgSO_4$, and filtered through a Celite column; solvents were removed under reduced pressure. The residue was chromatographed on silica gel to give **26b** (Et_2O:PE = 90:10) and the starting complex **25**. After recrystallization in pentane complex, **26b** (111.2 mg, 0.43 mmol, 43% yield) was obtained as a pure yellow powder. Anal. Calcd for $C_{11}H_{10}DCrNO_3$; C, 51.16; H + $^1/_2$D, 4.26; N, 5.42. Found: C, 51.63; H + $^1/_2$D, 4.27; N, 5.13. MS (CI) (NH$_3$): cm^{-1} 259 (M + H)$^+$, 123 (M + H − Cr(CO)$_3$)$^+$. ^1H NMR (CDCl$_3$) $δ$ 5.58 (d, $H_{3,5}$, ^3J = 6.5 Hz), 4.77 (d, $H_{2,6}$, ^3J = 6.5 Hz).

Tricarbonyl[$η^6$-(N,N-dimethylamino)benzene]chromium (26a): **25** (287 mg, 1 mmol), THF (40 mL), $LiEt_3BH$ (1 M, 4 mL, 4 mmol), reflux 1 day, hydrolysis; complex **26a** (115.1 mg, 0.45 mmol, 45% yield). Spectrometric and analytical data were in agreement with those obtained with a standard sample. MS (CI) (NH$_3$): m/e 258 (M + H)$^+$, 122 (M + H − Cr(CO)$_3$)$^+$.

($η^6$-Anisole)tricarbonylchromium (11) and ($η^6$-N,N-dimethylaniline)Cr(CO)$_3$ (26a): **25** (143.5 mg, 0.5 mmol), THF (10 mL), $LiEt_3BH$ (1 M, 2.5 mL, 2.5 mmol), stirring 3 h at room temperature, CF_3CO_2H (2 mL), THF (2 mL). The composition of the yellow residue (133.3 mg) was obtained by ^1H NMR spectroscopy and based on comparison with reference sample ^1H NMR spectra. According to ^1H NMR spectra respective yields were as follows: **11**, 34% (41.8 mg, 0.17 mmol); **26a**, 24% (30.8 mg, 0.12 mmol).

General Procedure for Hydrodeamination Reactions.
To a solution of (η^6-N,N-dimethylaminoarene)tricarbonyl-
chromium in THF was added a solution of LiEt$_3$BR (R = H or
D) in THF. The resulting mixture was stirred for several
hours at room temperature and injected via a syringe to a
solution of CF$_3$CO$_2$H in THF. During the injection an exo-
thermic reaction occurs that turns the solution to deep red and
after a few seconds to yellow. To the resulting solution was
added a concentrated aqueous solution of NaOH. The mixture
was extracted with Et$_2$O, and the organic phase was washed
with water and brine, dried over Na$_2$SO$_4$ and KOH pellets,
and filtered through a Celite column; solvents were removed
under reduced pressure. The residue was chromatographed
on silica gel.

**Tricarbonyl(η^6-monodeuteriobenzene)chromium (12-
D):** (η^6-*N,N*-dimethylaniline)Cr(CO)$_3$ (126.4 mg, 0.5 mmol),
THF (9 mL), LiEt$_3$BD (1 M, 3 mL, 3 mmol), stirring 24 h. CF$_3$-
CO$_2$H (1.5 mL), THF (1 mL); complex 12-D (25 mg, 0.12 mmol,
24% yield). Anal. Calcd for C$_9$H$_5$DCrO$_3$: C, 50.16; H + $^1/_2$D,
2.80. Found: C, 50.06; H, 2.90. MS (CI) (NH$_3$): *m/e* 233 (M
+ H + NH$_3$)$^+$, 216 (M + H)$^+$.

**Tricarbonyl(η^6-monodeuteriotoluene)chromium (6-*o*,
6-*m*):** 27a (271 mg, 1 mmol), THF (15 mL), LiEt$_3$BD (1 M, 3
mL, 3 mmol), stirring 25 h at room temperature, CF$_3$CO$_2$H
(2.5 mL), THF (1 mL); complexes 6-*o* and 6-*m* (52 mg, 0.23
mmol, 23% yield). The composition of the mixture was
obtained by analysis of ^{1}H NMR signals intregration values
(*I*) of H$_{3,5}$ and H$_{2,4,6}$ and according to ^{13}C NMR spectra for the
position of deuterium on the aromatic cycle. Values were as
follows: *I* = 3.0 (H$_{3,5}$), *I* = 4.6 (H$_{2,4,6}$). Consequently, the
composition (molality) was 40% 6-*m* and 60% 6-*o*.

**Tricarbonyl(η^6-monodeuteriotoluene)chromium (6-*o*,
6-*m*) with CF$_3$SO$_3$H acid step:** 27a (271 mg, 1 mmol), THF
(10 mL), LiEt$_3$BD (1 M, 3 mL, 3 mmol), stirring 20 h at room
temperature, CF$_3$SO$_3$H (3 mL), THF (1 mL); complexes 6-*o*
and 6-*m* (52 mg, 0.23 mmol, 23% yield). The composition was
40% 6-*m* and 60% 6-*o*.

**Tricarbonyl(η^6-monodeuteriotoluene)chromium (6-o
or 6-*p* and 6-*m*):** 27b (271 mg, 1 mmol), THF (10 mL), LiEt$_3$-
BD (1 M, 3 mL, 3 mmol), stirring 21 h at room temperature,
CF$_3$CO$_2$H(2 mL), THF (1 mL); complexes 6-*o* or 6-*p* and 6-*m*
(18 mg, 0.078 mmol, 8% yield). The composition was 75% 6-*m*
and 25% 6-*p*.

**Tricarbonyl(η^6-monodeuterio-*tert*-butylbenzene)chro-
mium (8-*o*, 8-*m*):** 28 (313 mg, 1 mmol), THF (10 mL), LiEt$_3$-
BD (1 M, 5 mL, 5 mmol), stirring 24 h at room temperature,
CF$_3$CO$_2$H (3 mL), THF (1 mL); complexes 8-*o* and 8-*m* (22 mg,
0.08 mmol, 8% yield). Anal. Calcd for C$_{13}$H$_{13}$DCrO$_3$: C, 57.56;
H, 5.20. Found: C, 57.60; H, 5.19. ^{1}H NMR (CDCl$_3$): δ 5.52
(dd + d, H$_{2,6}$, ^3J = 6.5 Hz, ^4J = 1.0 Hz), 5.38 (t, H$_4$, ^3J = 6.0
Hz, ^4J = 1.0 Hz), 5.22 (td + dd, H$_{3,5}$, ^3J = 6.0 Hz, ^4J = 1.0 Hz),
1.30 (s, 9H, CH$_3$C). The composition was 6% 8-*m* and 94% 8-*o*.

**Tricarbonyl[η^6-deuterio(trimethylsilyl)benzene]chro-
mium (4-*p*, 4-*o*):** 29a (281 mg, 0,8 mmol), THF (20 mL), LiEt$_3$-
BD (1 M, 1.2 mL, 1.2 mmol), stirring 20 h at room temperature,
CF$_3$CO$_2$H (10 mL), THF (1 mL); complexes 4-*p* and 4-*o* (115
mg, 0.4 mmol, 47% yield). ^{1}H NMR (CDCl$_3$): δ 5.51 (t, H$_4$, ^3J
= 6.5 Hz), 5.41 (d, H$_{2,6}$, ^3J = 6.5 Hz), 5.16 (d + t, H$_{3,5}$, ^3J = 6.5
Hz), 0.28 (s, (CH$_3$)$_3$Si). The composition was 16% 4-*p* and 84%
4-*o*.

**Tricarbonyl[η^6-4-deuterio(trimethylsilyl)benzene]chro-
mium (4-*p*):** 29b (164 mg, 0.5 mmol), THF (15 mL), LiEt$_B$D

(1 M, 2.5 mL, 2.5 mmol), stirring 4.5 h at room temperature,
CF$_3$CO$_2$H (3 mL), THF (1 mL); complex 4-*p* (87 mg, 0.30 mmol,
61% yield).

**Synthesis of Tricarbonyl(η^5-cyclohexadienyl)chromi-
um Complexes.**[35] **General Procedure for the Prepara-
tion of Lithium Tricarbonyl(η^5-cyclohexadienyl)chro-
mium(0) Complexes.** To a solution of (η^6-arene)tricar-
bonylchromium was added a solution of LiEt$_3$BR (R = D or
H) in THF. The resulting solution was refluxed for 30 min
and cooled in liquid nitrogen; a mixture of toluene (10 mL)
and *n*-hexane (25 mL) was added to induce the formation of
two liquid phases. The upper phase was removed, and
additional *n*-hexane was added to wash the lower phase that
became rapidly a brown-yellow oil. Solvents were removed
under 0.1 Torr vacuum to give an oily residue that was washed
with dry benzene, and the resulting lithium salt precipitated
as a pale yellow amorphous and pyrophoric powder when
exposed as it was to air. Elemental analyses and mass
spectroscopy failed to provide useful information given the high
reactivity of these complexes.

Li[(η^5-C$_6$H$_7$)Cr(CO)$_3$] (32a): complex 12 (1.26 g, 6 mmol),
THF (4 mL), LiEt$_3$BH (6 mL, 6 mmol); complex 32a (1.3 g, 5.8
mmol, 97% yield).

Li[(η^5-C$_6$H$_6$D)Cr(CO)$_3$] (32b): complex 12 (1.26 g, 6 mmol),
THF (4 mL), LiEt$_3$BD (6 mL, 6 mmol); complex 32b (1.30 g,
5.8 mmol, 97% yield).

Li[(η^5-1-*exo*-C$_{12}$H$_9$O)Cr(CO)$_3$] (30a): complex 18 (1.21 g,
4 mmol), THF (4 mL), LiEt$_3$BH (4 mL, 4 mmol); complex 30a
(0.69 g, 2.21 mmol, 55% yield).

**Preparation of tricarbonyl(η^5-cyclohexadienyl)(tri-
phenyltin)chromium(II) (Sn–Cr) complexes. [(η^5-C$_6$H$_7$)-
(CO)$_3$Cr–Sn(C$_6$H$_5$)$_3$] (33a):** THF (6 mL), 32a (304.8 mg, 1.4
mmol), −78 °C, THF (5 mL), Ph$_3$SnCl (580.9 mg, 1.5 mmol),
stirring for 1 h at −78 °C; complex 33a (418 mg, 0.74 mmol,
53% yield). MS (EI): *m/e* 566, 564, 562 (M (^{120}Sn, ^{118}Sn,
^{116}Sn))$^+$, 481 (M − 3CO)$^+$, 403−401 (Cr−SnPh$_3$)$^+$, 351 (^{120}Sn-
Ph$_3$)$^+$.

[(η^5-C$_6$H$_6$D)(CO)$_3$Cr–Sn(C$_6$H$_5$)$_3$] (33b): THF (6 mL), 32b
(304.8 mg, 1.4 mmol), −78 °C, saturated THF solution (5 mL)
of Ph$_3$SnCl (580.9 mg, 1.5 mmol); complex 33b (418 mg, 0.74
mmol, 53% yield).

[(η^5-1-*exo*-C$_{12}$H$_9$O)(CO)$_3$Cr–Sn(C$_6$H$_5$)$_3$] (31): THF (4 mL),
complex 30 (280 mL, 0.89 mmol), −78 °C, THF (4 mL), Ph$_3$-
SnCl (385.5 mg, 1 mmol); complex 31 (68.1 mg, 0.104 mmol,
11.6% yield). MS (EI): *m/e* 655, 653, 651 (M (^{120}Sn, ^{118}Sn,
^{116}Sn)).

Supplementary Material Available: Additional experi-
mental data, all bond distances and all bond angles, anisotropic
temperature factors, hydrogen atom positions, and important
least-squares planes (9 pages). Ordering information is given
on any current masthead page.

OM940602P

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(35) For complete analytical data, see: Reference 19.