A Polyfunctional Chromium Arene Complex: Synthesis and Derivatization of Tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0)

Peter C. Nirchio and Donald J. Wink*

Department of Chemistry, New York University, 4 Washington Place, New York, New York 10003

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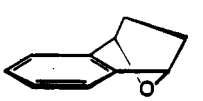
New routes to functionalized naphthalene and tetrahydronaphthalene complexes of tricarbonylchromium are described, based on the synthesis and derivatization of a complex of 1,4-epoxy-1,2,3,4-tetrahydronaphthalene. Chromium hexacarbonyl reacts with the epoxynaphthalene in butyl ether at reflux to give good yields of the corresponding chromium tricarbonyl arene complex. A single stereoisomer is formed, with the epoxy oxygen on the same side of the arene as the chromium tricarbonyl group, as confirmed by X-ray crystallography. Crystals of tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium form with space group symmetry $P2_1/c$ and cell constants a = 6.7006 (6) Å, b = 13.333 (2) Å, c = 13.258 (2) Å, and β = 96.00 (1)° with Z = 4. Refinement of 163 least-squares parameters using 1146 reflections with $I > 3.00\sigma(I)$ gave R = 0.035 and R_w = 0.048. The complexed epoxynaphthalene eliminates water to give a coordinated naphthalene, at room temperature in diethyl ether in the presence of HBF_4. The epoxynaphthalene complex is lithiated by *n*-BuLi at −30 °C, and quenching with isobutyraldehyde gives a mixture of isomers of alcohol complexes. One diastereomer of a 5-substituted complex predominates, and it is obtained pure in 50% yield by a single crystallization. The product, containing a 1-hydroxyisobutyl group, is dehydrated in a stepwise fashion, with the pendant alcohol converting to an olefin first and then, in the presence of excess acid, the epoxynaphthalene group converting to a naphthalene. The lithiated intermediate reacts with $CuBr{\cdot}SMe_2$ and then benzoyl chloride to give a 90:10 mixture of 5- and 6-benzoyl derivatives. The 5-benzoyl complex is purified by column chromatography. It cannot be dehydrated to give a stable chromium naphthalene complex, but dehydration by $BF_3{\cdot}Et_2O$ in air gives free 1-benzoylnaphthalene. Finally, the parent complex undergoes a ring-opening reaction with bromodimethylborane to yield, after treatment with benzylamine, a 1-hydroxy-4-(benzylamino) complex.

Arene complexes of the tricarbonylchromium fragment are widely used reagents in the synthesis of organic compounds, including several of biochemical interest.[1] Derivatives containing a polycyclic aromatic ligand such as naphthalene are especially interesting, for they are kinetically labile[2] and they are thermodynamically less stable than most monoarene derivatives.[3] This makes them useful in a host of stoichiometric[4] or catalytic[5] reactions. Very good results in the direct attack of nucleophiles on a coordinated naphthalene[6] and in the utilization of lithiated naphthalene intermediates as nucleophiles[7] for the synthesis of complexes of simple naphthalene derivatives have also been reported. However, the lability of naphthalene complicates photolytic substitution of carbon monoxide in a tricarbonyl complex to give $Cr(CO)_2L(\eta^6$-naphthalene) derivatives,[5f,g] a reaction that is usually facile in the case of monoarene derivatives.[8] In that connection we have developed the chemistry of chromium carbonyl complexes of a simple monoaromatic ligand, 1,4-epoxy-1,2,3,4-tetrahydronaphthalene (1), which serves as a source



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of "protected naphthalene" for photolytic substitution reactions.[9] This paper reports the synthesis and some of the reactivity of the parent chromium tricarbonyl complex, which reacts in several different ways to give unusual naphthalene derivatives.

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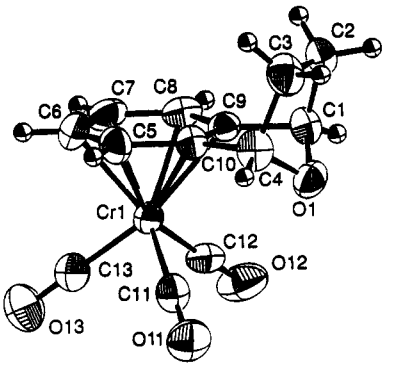

Figure 1. ORTEP[14] drawing of the epoxynaphthalene complex with thermal ellipsoids drawn at the 50% probability level.

Table I. Experimental Details for the Crystallographic Study

A. Crystal Data	
empirical formula	$CrC_{13}H_{10}O_4$
fw	282.22
cryst syst	monoclinic
lattice params	
a, Å	6.7006 (6)
b, Å	13.333 (2)
c, Å	13.258 (2)
β, deg	96.00 (1)
V, Å^3	1178.0 (3)
space group	$P2_1/c$ (No. 14)
Z	4
B. Intensity Measurements	
F_{000}	576
μ(Cu Kα), cm^{-1}	81.68
diffractometer	Rigaku AFC6
radiation (λ, Å)	Cu Kα (1.54178), graphite-monochromated
temp, °C	25
$2\theta_{max}$, deg	110.0
data collected	$+h,+k,\pm l$
no. of rflns measd	1718
no. of unique rflns (R_{int})	1563 (0.080)
transmissn factors for abs cor	0.85–1.32
C. Structure Solution and Refinement	
no. of observns ($I > 3\sigma(I)$)	1146
no. of variables	163
no. of observns/variable	7.0
residuals, %	R = 3.5, R_w = 4.3
goodness of fit	1.38
max peak in final diff map, e Å^{-3}	0.22
function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$, $w = 4F_o^2/\sigma^2(F_o)$

Results and Discussion

Synthesis, Characterization, and Dehydration of $Cr(CO)_3(\eta^6$-1,4-epoxy-1,2,3,4-tetrahydronaphthalene). The epoxynaphthalene[10] compound 1 is available from commercial sources or from the Diels–Alder reaction of furan and benzyne followed by hydrogenation.[11] It reacts with chromium hexacarbonyl under standard conditions[12] to give yellow crystalline product in 84% recrystallized yield (eq 1). The complex is as stable as other simple

$$Cr(CO)_6 + \underset{1}{C_{10}H_{10}O} \xrightarrow[Bu_2O/THF]{} Cr(CO)_3(\eta^6\text{-}C_{10}H_{10}O) + 3CO \quad (1)$$

(10) The compound 1 will be referred to trivially in this paper as "epoxynaphthalene". The corresponding 1,4-epoxy-1,4-*dihydro*naphthalene compound is also available and is the subject of other experiments in our laboratories.

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Table II. Positional and Isotropic Thermal Parameters for $Cr(CO)_3(\eta^6$-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)

atom	x	y	z	B(eq), Å^2
Cr1	0.0251 (1)	0.13447 (5)	0.15757 (5)	2.86 (3)
O1	−0.0342 (5)	−0.0228 (2)	0.3585 (2)	3.8 (1)
O11	0.2471 (6)	−0.0564 (3)	0.1340 (3)	5.0 (2)
O12	0.3889 (6)	0.2102 (3)	0.2836 (3)	5.7 (2)
O13	0.1947 (7)	0.2065 (4)	−0.0281 (3)	7.9 (3)
C1	−0.1036 (7)	0.0734 (4)	0.3900 (3)	3.4 (2)
C2	−0.3061 (7)	0.0459 (4)	0.4275 (3)	4.1 (2)
C3	−0.3754 (8)	−0.0395 (4)	0.3538 (4)	4.6 (3)
C4	−0.2039 (8)	−0.0442 (3)	0.2870 (4)	3.8 (2)
C5	−0.2809 (7)	0.0707 (4)	0.1202 (3)	3.8 (2)
C6	−0.2797 (7)	0.1702 (4)	0.0884 (4)	4.3 (3)
C7	−0.2166 (7)	0.2467 (4)	0.1564 (4)	4.1 (2)
C8	−0.1517 (7)	0.2256 (3)	0.2572 (4)	3.5 (2)
C9	−0.1510 (6)	0.1259 (3)	0.2894 (3)	2.8 (2)
C10	−0.2155 (6)	0.0490 (3)	0.2226 (3)	3.0 (2)
C11	0.1596 (8)	0.0174 (4)	0.1425 (3)	3.5 (2)
C12	0.2499 (7)	0.1806 (4)	0.2337 (4)	3.6 (2)
C13	0.1281 (8)	0.1792 (4)	0.0445 (4)	4.7 (3)

Table III. Intramolecular Bond Distances (Å) and Angles (deg) for $Cr(CO)_3(\eta^6$-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)

Cr1–C5	2.227 (5)	O13–C13	1.162 (6)
Cr1–C6	2.202 (5)	C1–C2	1.538 (7)
Cr1–C7	2.204 (5)	C1–C9	1.511 (6)
Cr1–C8	2.225 (4)	C2–C3	1.540 (7)
Cr1–C9	2.211 (4)	C3–C4	1.524 (7)
Cr1–C10	2.220 (4)	C4–C10	1.505 (6)
Cr1–C11	1.824 (5)	C5–C6	1.393 (7)
Cr1–C12	1.830 (6)	C5–C10	1.412 (6)
Cr1–C13	1.815 (5)	C6–C7	1.397 (7)
O1–C1	1.441 (5)	C7–C8	1.391 (7)
O1–C4	1.431 (5)	C8–C9	1.396 (6)
O11–C11	1.156 (5)	C9–C10	1.393 (6)
O12–C12	1.154 (5)		
C11–Cr1–C12	87.7 (2)	C3–C4–C10	107.3 (4)
C11–Cr1–C13	87.4 (2)	C6–C5–C10	118.3 (4)
C12–Cr1–C13	89.0 (2)	C5–C6–C7	120.7 (4)
C1–O1–C4	96.4 (3)	C6–C7–C8	121.1 (5)
O1–C1–C2	101.7 (4)	C7–C8–C9	118.5 (4)
O1–C1–C9	101.6 (3)	C1–C9–C8	134.8 (4)
C2–C1–C9	106.6 (4)	C1–C9–C10	104.1 (4)
C1–C2–C3	100.9 (4)	C8–C9–C10	121.0 (4)
C2–C3–C4	101.8 (4)	C4–C10–C5	135.0 (4)
O1–C4–C3	101.7 (4)	C4–C10–C9	104.6 (4)
O1–C4–C10	101.6 (4)	C5–C10–C9	120.3 (4)

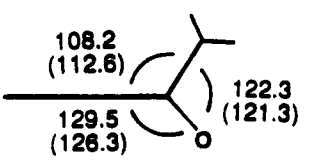


Figure 2. Comparison of the interplanar angles for the experimental structure of the coordinated ligand with (in parentheses) those calculated for free 1,4-epoxy-1,2,3,4-tetrahydronaphthalene.

arene complexes of $Cr(CO)_3$ and is not decomposed, for example, in the coordinating solvents that rapidly destroy $Cr(CO)_3$(naphthalene).[6b] It is also more stable in air than the naphthalene complex.

An X-ray diffraction analysis shows that the epoxy oxygen and the $Cr(CO)_3$ groups are on the same side of the ring (Figure 1).[13] Experimental details for the crystal

(13) There is an unfortunate problem in nomenclature here. From the standpoint of substitution on a bicyclo[2.2.1] skelton (which is appropriate for the epoxynaphthalene) the $Cr(CO)_3$ group is on the exo face. However, from the standpoint of the metal the face of the π-ligand that it coordinates to is referred to as the endo face. The latter nomenclature will be used throughout this paper.

(14) Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

structure study are summarized in Table I, positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table II, and intramolecular bond distances and angles are collected in Table III. The solid-state structure of the complex contains the epoxynaphthalene ligand in a geometry that is essentially undistorted from the minimum-energy structure calculated for the free ligand with use of MM2 methods.[15] This includes the angles about the planes defined by the six coordinated carbons, the four noncoordinated carbons, and the epoxy oxygen and the 1- and 4-carbons (Figure 2). The observed structure is also similar to that determined for a coordinated benzonorbornene ligand.[16] This includes a "pinching" of the ortho groups toward one another because of strain in the epoxy ring system, as shown by the angles C4–C10–C9 = 104.6 (4)° and C1–C9–C10 = 104.1 (4)° instead of an unstrained angle of 120°. The $Cr(CO)_3$ unit is oriented so as to eclipse the centers of C–C bonds on the arene, including the bond opposite from the ring fusion. The exclusive formation of the endo isomer is explained by initial coordination of the epoxy oxygen followed by intramolecular coordination of the arene.[17] Related observations about the directing influence of an olefin group with benzonorbornadiene type molecules have been made.[18]

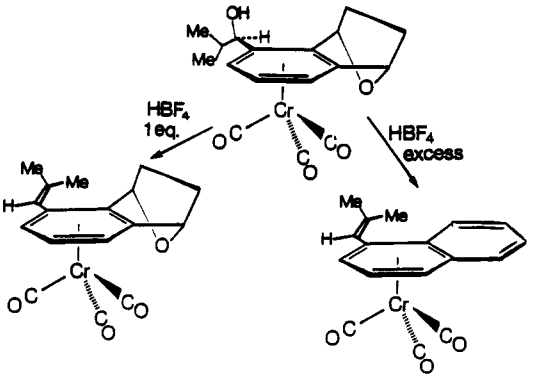
The chromium-coordinated epoxynaphthalene moiety still readily eliminates water under acidic conditions (HBF_4 in ether, toluene, and CH_2Cl_2—ether is slowest and cleanest), producing tricarbonyl(naphthalene)chromium(0) in 47% yield after purification by column chromatography to remove a small amount of decomposition produce (eq 2).

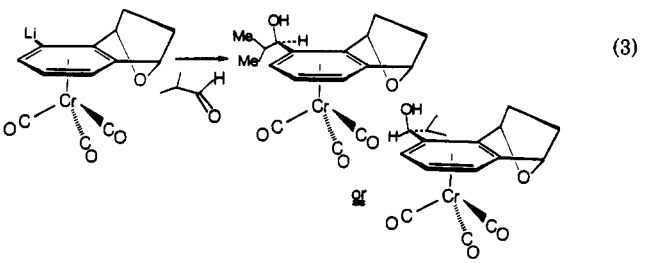
$$Cr(CO)_3(\eta^6\text{-}C_{10}H_{10}O) \xrightarrow[HBF_4/Et_2O]{} Cr(CO)_3(\eta^6\text{-}C_{10}H_8) + H_2O \quad (2)$$

Lithiation and Functionalization of the Coordinated Ring. Facile lithiation, often involving considerable regioselection,[19] is one of the fundamental reactions of chromium-coordinated arenes. A variety of manipulations can be performed with lithiated monoarene complexes, including transmetalation with copper salts.[20] Reports of lithiation of chromium-coordinated naphthalenes indicate that they too react efficiently with simple electrophiles,[7] though there are no reports of transmetalation reactions from chromium complexes of metalation naphthalenes to our knowledge. The protected naphthalene strategy provides an alternative to simple lithionaphthalene complexes.

Lithiation of $Cr(CO)_3(\eta^6$-1,4-epoxy-1,2,3,4-tetrahydronaphthalene) is accomplished by a *n*-BuLi in THF at −30 °C with use of the conditions reported by Card and Trahanovsky.[19f] The lithiated intermediate reacts with isobutyraldehyde to give, after recrystallization, a diastereomerically pure complex with the 1-hydroxyisobutyl group in the 5-position (eq 3). Chromatography can be

Scheme I. Stepwise Conversion of the Epoxynaphthalene Alcohol to the Butenylnaphthalene Complex





(3)

used to free material of a small amount of contaminating 5-isobutenyl complex (vide infra). Examination of the crude product mixture indicates that the other diastereomer and the 5-substituted derivative are present at about 10% of the amount of the major product.

For the major product, a single pair of doublets appears in the ^1H NMR spectra for the diastereotopic methyl groups of the isopropyl side chain. These are coupled to a multiplet that in turn is coupled to a triplet at δ 4.14. This triplet is assigned to the methine proton α to the coordinated ring. It is coupled to both the methine proton of the $CHMe_2$ group and to the OH proton; addition of D_2O to the sample causes the signal to revert to a doublet at the same time as the OH resonance disappears. A single α-methine proton resonance demonstrates that the product is diastereomerically pure. Unfortunately, we have been unable to obtain X-ray-quality crystals of the alcohol complex to determine which diastereomer does prevail and nuclear Overhauser effect (NOE) experiments are ambiguous.

The regioselection (discussed in more detail below) and diastereoselection in this reaction are remarkably high.[21] Diastereoselection in reactions of chromium arene complexes is well-known, but is has focused on selective complexation[4] or synthesis[22] of materials with one π-face on the metal utilizing chiral groups α to the coordinated ring. Semmelhack and co-workers showed that modest diastereoselection (60:40) can be achieved with lithiated anisole derivatives,[19g] while Widdowson and co-workers reported

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(21) We have found that the corresponding electrophilic attack by benzaldehyde is much less specific (ca. 60:40 mixture): Wink, D. J.; Teli, S., research in progress.
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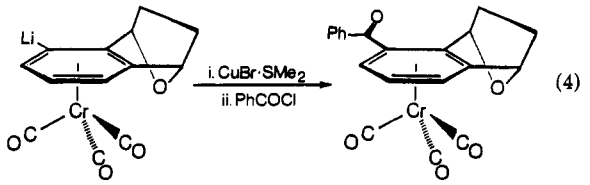
no diastereoselection in the addition of aldehydes to lithiated indole complexes.[19d] Treichel and Kirss[7c] did report the reaction of acetaldehyde with a lithiated naphthalene complex but made no mention of stereoselection. The occurrence of diastereoselection with the lithiated epoxynaphthalene complex is easily explained by the steric environment; the $Cr(CO)_3$ group will cause the aldehyde to attack from the exo face of the arene, and the backbone of the epoxynaphthalene group should force the isopropyl group of the aldehyde to lie over the 6-carbon of the coordinated ring.

The alcohol product is dehydrated by acid in a stepwise manner. The alchol eliminates water in the presence of 1 equiv of HBF_4 to give a butenyl side group. Dehydration of the epoxynaphthalene group also requires excess acid (Scheme I). The vinyl products in both cases exhibit a single vinyl proton resonance and a pair of CH_3 groups.

Transmetalation with Copper(I) Bromide. Conversion of lithiated species into copper reagents permits the use of many other electrophiles.[20] This is shown in the case of the lithiated epoxynaphthalene species by reaction with $CuBr{\cdot}SMe_2$ and then addition of benzoyl chloride to give a ca. 90:10 mixture of 5- and 6-benzoyl derivatives (eq 4). These are separated from each other by chromatography with ether/hexane, and the 5-benzoyl derivative is separated from a small amount of starting material by another column with methylene chloride/hexane. The product of interest, containing a 5-benzoyl group, is obtained in 57% yield as a red oil that solidifies on standing to an orange solid.

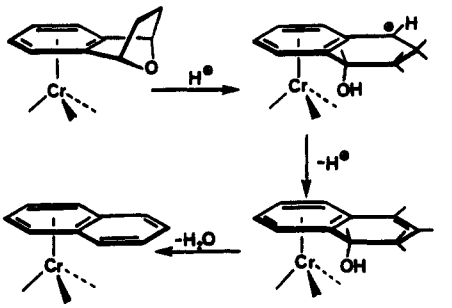


(4)

The 5-benzoylnaphthalene complex reacts with BF_3 or HBF_4 in ether or methylene chloride to give highly colored green solutions in a matter of seconds that gradually turn blue and then red. Quenching of an aliquot from these solutions in the first minutes of the reaction regenerates the orange color of the starting material, and TLC analysis indicates that the starting material is the only species present. With time, however, the reaction produces other species, but we have thus far been unable to isolate and identify any chromium-containing products, including the expected benzoylnaphthalene derivatives. Rather, a substantial amount of *free* 1-benzoylnaphthalene is formed in all cases. Its yield is maximized by dehydration with neat $BF_3{\cdot}Et_2O$ in air. A 76% yield of benzoylnaphthalene, identified by comparison with commercially acquired material, is obtained. The difference in the dehydration reaction of the benzoyl complex is probably due to complexation of the acid by the carbonyl group. This would account for the dramatic and initially reversible color change. It may also explain the lability of the benzoylnaphthalene complexes that are formed by slow dehydration of the epoxy ring.

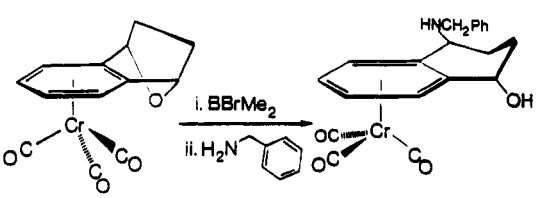
The regioselectivity of metalation in these reactions indicates a strong preference for deprotonation of the 5-position, α to the ring junction. This preference is the opposite of that seen for complexed naphthalene, where the lithiation proceeds predominantly or exclusively to the β-position.[7] A more useful comparison is with lithiation of other ortho-disubstituted monoarenes. For example, Kündig and co-workers have shown that coordinated benzocyclobutane is exclusively deprotonated at the α-position while the related reaction with complexed indane yields mostly β-deprotonation.[23] The difference is ascribed to the increased strain of the cyclobutane group vs that of the cyclopentane group, and we presume that the strain present in epoxynaphthalene exerts a similar α-activating influence.

Scheme II. Probable Mechanism of Dehydration of the Coordinated 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene Ring



Electrophilic Opening of the Epoxynaphthalene Ring. The dehydration reaction probably proceeds by the mechanism shown in Scheme II. It is tempting to think that the intermediate carbocation could be captured by an appropriate nucleophile, but a series of preliminary reactions, patterned after the conditions employed in nucleophilic attack on carbocations generated from α-alcohols and acetates,[24] gave either no reactions (e.g., H_2SO_4 in methanol) or simple conversion to the naphthalene complex (HBF_4 in anisole). This is undoubtedly because the loss of proton from any intermediate cation is more rapid than nucleophilic attack. Similarly, direct nucleophilic attack (trialkylborohydride in THF) apparently gives only attack on the arene, not ring opening of the epoxy group.[25]

The only method that we have found capable of functional ring opening of the epoxy ring uses the bifunctional reagent $BBrMe_2$. This has been developed by Guindon and co-workers for the selective opening of cyclic ethers, including tetrahydrofurans and even free epoxytetrahydronaphthalene,[26] in which case the product is 1-hydroxy-4-bromotetrahydronaphthalene. Though this species is unstable with respect to aromatization, they found that the bromo compound can be captured by amine nucleophiles to give stable disubstituted tetrahydronaphthalenes. This ring-opening reaction is compatible with the presence of the tricarbonylchromium moiety, and the α-bromo group can still be selectively substituted by amines. Reacting the parent chromium epoxynaphthalene complex $BBrMe_2$ in THF followed by quenching with benzylamine gives far yields of the *trans*-1-hydroxy-4-(benzylamino)tetrahydronaphthalene derivative (eq 5).



(5)

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Table IV. ^{1}H NMR Data[a]

ligand	coordinated ring			uncoordinated ring			substituent		
	assignt	δ	mult (J)	assignt	δ	mult (J)	assignt	δ	mult (J)
$C_{10}H_{10}O$	5, 8	4.31	dd (2.7, 4.2)	1, 4	4.47	dd (1.5, 2.4)	N/A[b]		
	6, 7	4.63	dd (2.7, 4.2)	2c, 3c	1.48	m			
				2t, 3t	0.76	m			
$C_{10}H_9O(CHOHCHMe_2)$	6	4.99	d (6.3)	1	4.44	d (4.5)	OH	1.56	d (3.9)
	7	4.35	t (6.3)	2c, 3c	1.5	m	α	4.14	t (3.6)
	8	4.49	d (6.0)	2t, 3t	0.8	m	β	1.4	m
				4	4.58	d (4.5)	CH_3	0.82	d (6.9)
							CH_3	0.67	d (6.9)
$C_{10}H_9O(CH{=}CMe_2)$	6	4.47	d (3.6)	1	4.54	d (4.5)	α	5.87	s
	7	4.60	t (3.6)	2c, 3c	1.50	m	E-CH_3	1.52	s
	8	4.70	d (3.6)	2t, 3t	0.82	m	Z-CH_3	1.44	s
				4	4.80	d (4.5)			
$C_{10}H_7(CH{=}CMe_2)$	2	5.29	d (6.6)	5	7.00	m	α	6.49	s
	3	4.81	t (6.4)	6, 7	6.84	m	E-CH_3	1.66	s
	4	4.97	d (6.2)	8	7.48	m	Z-CH_3	1.40	s
$C_{10}H_9O(COC_6H_5)$	6	4.98	d (6.3)	1	4.42	d (4.8)	o	7.81	d (6)
	7	4.07	t (6.3)	2c	1.47	m	m, p	7.05	m
	8	4.78	d (6.3)	2t	0.79	m			
				3c	1.70	m			
				3t	1.24	m			
				4	5.67	d (5.1)			
$C_{10}H_7(OH)(NHCH_2C_6H_5)$	5	5.12	d (6.6)	1	3.99	d of t (4.7, 9.4, 9.4)			
	6	4.58	t (6.4)	2c	1.24	m	OH	1.30	d (9.3)
	7	4.27	t (6.3)	2t	1.60	m	NH	0.44	qu (7.8)
	8	5.28	d (6.4)	3c	0.71	m	CH_2	3.19	m (J_{NH} = 7.6)
				3t	1.60	m	C_6H_5	7.25–7.05	m
				4	3.43	d of t (5.4, 8.8, 8.8)			

[a] Nomenclature for protons on the 2- and 3-positions of the tetrahydronaphthalene complexes relies on assignment as cis (c) or trans (t) to the oxygen on the 1-position. All coupling constants are in Hz with a resolution of 0.3 Hz. [b] N/A = not applicable.

The trans stereochemistry is assigned on the basis of the observation of NOE enhancements of the peaks for the protons on the 5- and 8-positions of the coordinated ring during irradiation of the OH and NH protons, respectively. Much weaker enhancements of the protons on the 5- and 8-positions are seen when the protons on the 1- and 4-positions are irradiated. This can be explained by assuming the 1- and 4-positions have the NH and OH groups in mutually trans equatorial positions. This is chemically reasonable because the boron reagent is known to add the bromine cis to the alcohol and, presumably, nucleophilic attack of benzylamine proceeds by an S_N2 mechanism with inversion of configuration at the benzylic position.[26]

Conclusion. The development of chromium arene chemistry has reached a point where substrates with versatile functionality will be increasingly important in developing more sophisticated and versatile applications. The simple substrate 1,4-epoxy-1,2,3,4-tetrahydronaphthalene has now been shown to possess multiple reactivity in the form of selective lithiation, electrophilic attack, dehydration, and ring-opening reactions, all of which, in principle, can be incorporated into the synthesis of elaborate polycyclic products.

Experimental Section

General Considerations. All manipulations were conducted with use of standard inert-atmosphere techniques, except where noted. All elemental analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. Chromium hexacarbonyl (Pressure Chemical Co.) was used as supplied. Benzoyl chloride (Mallinkcrodt Co.) was distilled from KOH and stored under nitrogen. Isobutyraldehyde, benzylamine, tetrafluoroboric acid–diethyl ether complex, butyl ether, bromodimethylborane, *n*-butyllithium, $CuBr{\cdot}SMe_2$, and 1,4-epoxy-1,2,3,4-tetrahydronaphthalene were purchased from Aldrich Chemical Co. and used as supplied. Diethyl ether and tetrahydrofuran (both Fisher Chemical Co.) for reactions were dried over sodium benzophenone and distilled. Flash chromatography columns were prepared in air and run under nitrogen pressure with 230–400 mesh silica gel with use of solvents as supplied.

All spectral data were obtained in C_6H_6 or C_6D_6, except where indicated. NMR spectra were obtained on General Electric QE-300 and GN-300 spectrometers. All spectra were referenced to resonances of residual protons in the deuterated solvent. Data for important new compounds are listed in Tables IV and V. Assignments were accomplished through a combination of COSY and 1-dimensional NOE experiments. Key data for the latter treatment are given with each compound, with use of the following shorthand notation: irradiated resonance (assignment) → affected resonance (percent enhancement, assignment).

Synthesis of Tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0). A mixture of 11.9 g (54.1 mmol) of chromium hexacarbonyl, 6.0 g (41.1 mmol) of 1 in 400 mL of Bu_2O, and 40 mL of THF was carefully deoxygenated and then heated at reflux with magnetic stirring for 21.5 h. The mixture was cooled, and the THF was removed in vacuo at room temperature. The solution was heated (ca. 65 °C) under nitrogen and filtered while hot. Butyl ether was removed in vacuo to give spectroscopically pure (^{1}H NMR) yellow microcrystalline powder (10.7 g, 92% with respect to 1). Yield after recrystallization from butyl ether: 9.77 g, 84%. IR: 1971 (vs) 1898 (vs) cm^{-1}. ^{1}H NOE data used for assignment: δ 4.31 ($H_{5,8}$) → δ 4.47 (9%, $H_{1,4}$); δ 1.48 ($H_{2c,3c}$) → δ 4.47 (12%, $H_{1,4}$). Anal. Calcd for $C_{13}H_{10}CrO_4$: C, 55.33; H, 3.57. Found: C, 55.25; H, 3.71.

Dehydration of the (Epoxytetrahydronaphthalene)chromium Complex. A Schlenk tube was charged with the epoxynaphthalene complex (0.750 g, 2.66 mmol) and 5.0 mL of Et_2O. The heterogeneous mixture was thoroughly deoxygenated, and $HBF_4{\cdot}Et_2O$ (Aldrich, 0.25 mL) was added via syringe. The mixture was stirred 20.5 h, and then 2 mL of a 2 M aqueous solution of K_2CO_3 was injected. After 20 min the flask was opened up to air and the layers were separated. The ether layer was dried with $MgSO_4$, filtered, and purified by column chromatography (silica, 4:1 hexane–ether). Removal of solvent gave pure (^{1}H NMR) crystalline tricarbonyl(η^6-naphthalene)chromium(0) (0.331 g, 47%), identified by comparison of the ^{1}H NMR spectrum (multiplets at δ 6.85, 6.71, 5.23, and 4.61) with that of material

Table V. ^{13}C NMR Data

ligand	coordinated ring		uncoordinated ring		substituent	
	assignt	δ	assignt	δ	assignt	δ
$C_{10}H_{10}O$	5–8	89.4, 86.1	1, 4	76.9	CO	233.3
	4a, 8a	114.2	2, 3	27.3		
$C_{10}H_9O(CHOHCHMe_2)$	5	111.2	1, 4	77.1, 75.4	CO	233.6
	6–8	90.0, 86.9, 85.5	2, 3	27.1, 27.0	α	73.5
	4a, 8a	113.6, 113.1			β	35.1
					CH_3'	20.0
					CH_3''	14.9
$C_{10}H_9O(CH{=}CMe_2)$	5	103.7	1, 4	77.2, 75.9	CO	233.7
	6–8	90.2, 89.8, 83.7	2, 3	27.3, 27.1	α	119.0
	4a, 8a	114.5, 113.1			β	140.6
					CH_3'	26.2
					CH_3''	19.5
					CO	232.3
$C_{10}H_7(CH{=}CMe_2)$	2–4	93.9, 91.9, 89.9	5–8	129.2–126.5	α	120.2
	1, 4a, 8a	105.6, 105.4, 104.0			β	140.6
					CH_3'	25.9
					CH_3''	19.2
$C_{10}H_9O(COC_6H_5)$	5	93.5	1, 4	77.7, 76.4	CO	231.6
	6–8	95.1, 88.7, 86.8	2, 3	26.8, 26.1	C=O	194.3
	4a, 8a	114.7, 112.7			ipso-C_6H_5	137.4
					o,m-C_6H_5	129.0, 128.7
					p-C_6H_5	132.4
$C_{10}H_7(OH)(NHCH_2C_6H_5)$ (obtained in $(CD_3)_2CO$)	5–8	94.2, 92.3, 92.2, 91.2	1	65.7	CO	234.0
	4a, 8a	116.3, 114.3	2, 3	30.8, 29.8	CHOH	65.7
					CHNH	54.3
					CH_2NH	49.9
					C_6H_5	140.9, 128.1, 126.6

obtained by the direct reaction of naphthalene and $Cr(CO)_6$.[6b] Improved yields (60%) are obtained when the reaction is run at 36 °C.

Synthesis of Tricarbonyl(η⁶-1,4-epoxy-5-(1-hydroxyisobutyl)-1,2,3,4-tetrahydronaphthalene)chromium(0). A solution of 0.50 g (1.8 mmol) of the chromium epoxynaphthalene complex in 20 mL of THF was cooled in a bath at −30 °C. A solution of *n*-BuLi (1.5 mL, 1.6 M in hexane, 2.4 mmol) was added, and the mixture was stirred for 10 min. Isobutyraldehyde (0.9 mL, 10 mmol) was added, and the reaction mixture was stirred overnight as the bath was warmed to room temperature. The solvent was removed in vacuo, and ca. 30 mL of ether was added in air. The organic layer was extracted with 20 mL of saturated $NaHCO_3$ and separated. The aqueous layer was extracted with 3 × 20 mL of ether, and then the combined ether extracts were washed with 3 × 30 mL of water. The combined organic layers were dried with K_2CO_3 and concentrated. Ether (ca. 10 mL) was added, and if necessary, the solution was filtered; octane (20 mL) was then added, and a portion of the ether was removed in vacuo until solids began to appear. The mixture was chilled overnight to give yellow microcrystals, which were combined with a second crop obtained after further concentration of the supernatant. Combined yields: 0.32 g, 50% (contaminated with ca. 2% tricarbonyl(η⁶-1,4-epoxy-5-isobutenyl-1,2,3,4-tetrahydronaphthalene)chromium(0)). IR: 1975, 1895 cm^{-1}. ^1H NMR: the peak at δ 1.56 (O*H*) is lost, and the peak at δ 4.14 (C*H*OH) becomes a doublet when the solution is shaken with D_2O. NOE data used for assignment: δ 4.14 (H_α) → 4.99 (4%, H_6); δ 4.14 (H_α) → 4.58 (10%, H_4). Anal. Calcd for $C_{17}H_{18}CrO_5$: C, 57.63; H, 5.12. Found: C, 58.29; H, 5.29.

Partial Dehydration of the 5-(1-Hydroxyisobutyl) Complex To Give Tricarbonyl(η⁶-1,4-epoxy-5-isobutenyl-1,2,3,4-tetrahydronaphthalene)chromium(0). A solution of the alcohol product (0.150 g, 0.42 mmol) was dissolved in 10 mL of ether in a pressure flask with a threaded Teflon stopcock and a magnetic stirbar. The solution was deoxygenated and frozen in liquid nitrogen, and then 85% $HBF_4{\cdot}Et_2O$ (100 μL, 0.85 g, 0.52 mmol) was added via syringe. The vessel was then subjected to two freeze–thaw cycles before being left to stir vigorously at 65 °C. After 17 h the cloudy yellow solution was cooled to room temperature and 3 mL of 2 M K_2CO_3 was added. The layers were separated, and the ether layer was dried over $MgSO_4$. The solution was decanted from the solids, and the solids were then washed with 3 × 3 mL of ether. The ether was removed under vacuum to give 67 mg of product (0.20 mmol, 47%). IR: 1968, 1892 cm^{-1}. ^1H NMR NOE data used for assignment: δ 5.87 (H_α) → δ 4.80 (6%, H_4); δ 1.52 (*E*-CH_3) → δ 5.87 (16%, H_α). Anal. Calcd for $C_{17}H_{16}CrO_4$: C, 60.72; H, 4.80. Found: C, 60.23; H, 4.84.

Synthesis of Tricarbonyl(η⁶-5-isobutenylnaphthalene)chromium(0) by Complete Dehydration. When a similar reaction was carried out with 0.10 g of the epoxynaphthalene alcohol and 780 μL of $HBF_4{\cdot}Et_2O$ (ca. 4.1 mmol), 49 mg of the corresponding vinylnaphthalene was obtained (0.15 mmol, 55%). IR: 1965, 1895, 1880, cm^{-1}. ^1H NMR NOE data used for assignment: δ 5.29 (H_4) → δ 7.00 (9%, H_5); δ 1.66 (*E*-CH_3) → δ 6.49 (16%, H_α). Anal. Calcd for $C_{17}H_{14}CrO_3$: C, 64.15; H, 4.43. Found: C, 63.97; H, 4.76.

Synthesis of Tricarbonyl(η⁶-5-benzoyl-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0). A solution of 1.06 g (3.2 mmol) of the chromium epoxynaphthalene complex in 20 mL of THF was cooled in a bath at −30 °C. A solution of *n*-BuLi (2.5 mL, 1.6 M in hexane, 4.0 mmol) was added, and the mixture was stirred for 10 min. The cooling-bath temperature was lowered to dry-ice temperature, and then, against a gentle stream of nitrogen, 0.80 g (3.9 mmol) of $CuBr{\cdot}SMe_2$ was added. The heterogeneous mixture was stirred in the dry-ice bath until almost all of the copper reagent had dissolved (about 1 h). Benzoyl chloride (1 mL, 1.2 g, 8.6 mmol) was added via syringe, and then the yellow solution was warmed slowly to room temperature overnight. Workup was done by opening the flask to air and treating the clear red solution with 50 mL of 1 M NaOH and 50 mL of ether. The mixture was stirred vigorously for 1 h, and then the layers were separated. The aqueous layer was extracted with 2 × 50 mL aliquots of ether, and the combined organic layers were dried with $MgSO_4$ and concentrated to a red oil. The oil was taken up in ether and chromatographed on a silica column with 1:3 ether–hexane; this separates the 5- and 6-benzoyl species. The 5-benzoyl fraction contained a small amount of starting epoxynaphthalene complex, which was separated by chromatography on silica with 1:1 methylene chloride–hexane. Removal of solvent left the spectroscopically pure 5-benzoyl complex as a red oil (0.70 g, 57%) that solidifed on standing. IR: 1980, 1920, 1920 cm^{-1} (Cr—CO1; 1655 cm^{-1} (C=O). ^1H NMR NOE data used for assignment: δ 4.78 (H_8) → δ 4.42 (3%, H_1). Anal. Calcd for $C_{20}H_{14}CrO_5$: C, 62.18; H, 3.65. Found: C, 61.19; H, 3.52. The 6-benzoyl complex has the following ^1H NMR spectrum: δ 7.70

d (d, *o*-H), 7.05 (m, *m,p*-H), 5.87 (s, 5-H), 4.43 and 4.35 (d, 6.6 Hz, 6- and 8-H), 4.46 and 4.21 (d, 3.9 Hz, 1- and 4-H), 1.45 (m, cis H's) 0.80 (m, trans H's).

Dehydration and Decomplexation of the 5-Benzoylepoxynaphthalene Complex. A sample of the 5-benzoylepoxynaphthalene complex (100 mg, 0.26 mmol) was stirred in 5 mL of BF_3-Et_2O in air overnight. The resulting orange-brown solution was diluted with 50 mL of ether and stirred vigorously with 200 mL of a buffer of ca. 0.5 M $NaHCO_3$–1.5 M Na_2CO_3. The layers were separated after 2 h, and the aqueous layer was extracted with 2 × 50 mL aliquots of ether. The combined organic layers, which are light pink, were concentrated to a light brown paste. This was extracted with hexane to give a colorless solution. Solvent was removed to give 46 mg (0.20 mmol, 76%) of 1-benzoylnaphthalene, identified by comparison of its ^1H NMR spectrum (δ 8.28 d, 7.80 d, 7.57 t, 7.28 d, 7.07 t, 6.95 t) with that of commercially obtained material (Pfalz and Bauer).

Synthesis of Tricarbonyl(η^6-*trans*-4-(benzylamino)-1-hydroxy-1,2,3,4-tetrahydronaphthalene)chromium(0). A solution of the epoxytetrahydronaphthalene complex (0.43 g, 1.5 mmol) in 10 mL of CH_2Cl_2 was cooled in an ice–water bath and treated with 25 μL of triethylamine and 300 μL of a 1:1 (v:v) solution of $BBrMe_2$ in CH_2Cl_2 (150 μL of $BBrMe_2$, 180 mg, 1.5 mmol). After 1 h 0.70 mL of NH_2CH_2Ph (ca. 7.0 mmol) was added to the clear lime green solution. The ice bath was removed, and the solution turned cloudy and then clear yellow. The mixture was opened to the air and quenched with 10 mL of H_2O and 10 mL of 2 M NaOH. Addition of ether generated two layers, which were separated; the aqueous layer was extracted with 2 × 20 mL aliquots of ether. The combined organic extracts were rinsed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (3:1 hexane–Et_2O, then Et_2O, then pure acetone) gave the product (0.24 g, 41%) after removal of solvent from the most polar fraction. IR: 1965, 1895 cm^{-1}. ^1H NMR NOE data used for assignment: δ 0.45 (NH) → δ 5.28 (5%, H_8). Anal. Calcd for $C_{20}H_{19}CrNO_4$: C, 61.69; H, 4.91; N, 3.60. Found: C, 62.23; H, 5.37; N, 3.61.

Crystallography of Tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0). Crystals of tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0) were grown by slow cooling of a butyl ether solution. Relevant experimental details and results are given in Tables I–III, and additional information is provided in the supplementary material. Structure solution was by Patterson methods in combination with DIRDIF.[27] An empirical absorption correction (DIFABS) was applied after isotropic refinement.[28]

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Supplementary Material Available: Listings of anisotropic thermal parameters and calculated positional and thermal parameters for hydrogen atoms, torsional angles for non-hydrogen atoms, and relevant least-squares planes (5 pages); a complete listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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