2.4

Product Class 4: Arene Organometallic Complexes of Chromium, Molybdenum, and Tungsten

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General Introduction

Arene complexes of chromium, molybdenum, and tungsten fall essentially into two categories.[1] The first are sandwich complexes of the type metal–bis(η^6-arene), and the second are of the type tricarbonylmetal–(η^6-arene) and derivatives thereof in which one or several of the carbonyl ligands are substituted by other ligands (alkenes, phosphines, etc.). Literature on arene and heteroarene complexes of these metals is abundant for chromium, but decreases sharply on going to molybdenum and particularly to tungsten. The primary reason for this lies in the more difficult access to the complexes of the heavier elements. The largest body of research covers reactions of (arene)tricarbonylchromium(0) complexes. Over the past 20 years these compounds have found wide application in catalysis and in organic synthesis. Recent work in the latter area focuses primarily on diastereoselective and enantioselective transformations of arenes.

Synthesis of Product Class 4

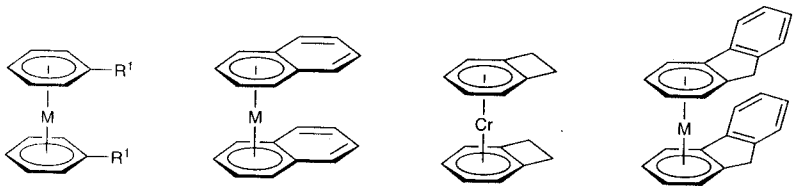
2.4.1 Method 1: Direct Synthesis of Metal–Bis(arene) Complexes via Metal Evaporation

The direct reaction of a metal with a ligand is conceptually the most straightforward synthetic route to homoleptic organometallic complexes containing the metal in the zero oxidation state. Strong metal—metal bonds in the bulk metal, the presence of oxide films on the metal, and unfavorable thermodynamics often render this route impossible. A solution to this problem is offered by metal-vapor synthesis whereby the metal vapor, consisting of atoms of transition metals, is generated and condensed with an excess of ligand before agglomeration to bulk metal can take place.[2] For arene sandwich complexes of group 6 metals this is the most versatile method, providing the sandwich complexes in yields up to 65% based on the amount of the metal evaporated.[3,4] Chromium can be sublimed at a useful rate for laboratory scale synthesis at a temperature of ca. 1200–1400 °C. The most accessible procedure consists of the use of a rotary apparatus in which the condenser and rotary seal parts of a commercial rotavapor are replaced by two electrodes and an improved rotary seal.[5,6] Chromium is evaporated from a resistively heated, insulated alumina crucible in the center of a 2-L flask containing the arene in an inert solvent (often methylcyclohexane) and externally cooled so as to maintain a vacuum of preferably $<1 \times 10^{-4}$ Torr in the flask. The metal vapor condenses and reacts with the arene in the film of the mixture carried over by rotation of the flask. Alternative apparatus has been used whereby the metal vapor and the arene are co-condensed on a liquid nitrogen cooled wall of a reactor under vacuum. This method has also been applied for the synthesis of molybdenum and tungsten sandwich complexes. As the temperatures required for the evaporation of these metals are much higher (2500 °C for Mo, 3300 °C for W), the synthesis apparatus for the use of these metals is more sophisticated and focused electron beam technology is used for the metal evaporation.[7] Mixed sandwich compounds can also be

for references see p 220

obtained by the co-condensation method. A selection of complexes **1–4** prepared by metal-vapor synthesis is shown in Scheme 1.

Scheme 1 Metal–Bis(arene) Complexes Prepared via Metal-Vapor Synthesis[2,8–18]



1 **2** **3** **4**

Complex	R¹	M	Ref	Complex	R¹	M	Ref
1	H	Cr	[2]	**1**	NMe_2	Mo	[12]
1	H	Mo	[8]	**1**	TMS	Cr	[17]
1	H	W	[9]	**1**	CN	Cr	[13]
1	Me	Cr	[10]	**2**	–	Cr	[14,15]
1	Me	Mo	[8]	**2**	–	Mo	[16]
1	Me	W	[8]	**3**	–	Cr	[17]
1	Cl	Cr	[11]	**4**	–	Cr	[18]
1	Cl	Mo	[12]	**4**	–	Mo	[18]
1	NMe_2	Cr	[11]	**4**	–	W	[18]

Bis(η⁶-naphthalene)chromium(0) (2, M = Cr):[14]

CAUTION: *The chromium particles deposited on the crucible insulation material and on the electrodes are pyrophoric. Inflammable liquids (e.g., cooling bath) must be kept at a safe distance.*

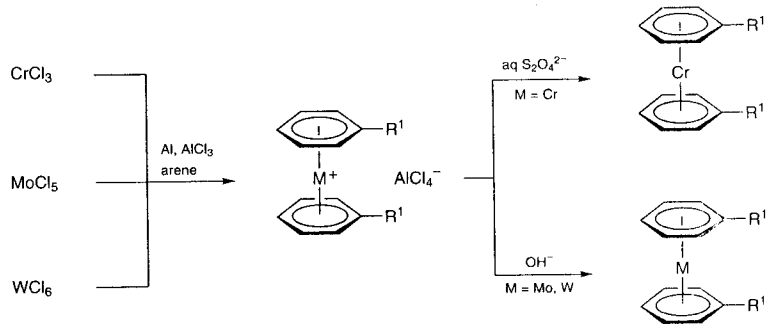
Cr metal (0.98 g, 18.8 mmol) was evaporated over a period of 2.5 h from an insulated Al_2O_3 crucible (1 mL) with imbedded Mo wire (1.2 mm diameter), resistance heated via water-cooled copper electrodes, and using a current of 31 A at 4.2 V. The Cr vapor was condensed into a cold (–80 °C) soln of naphthalene (10.0 g, 78 mmol) in dry diglyme (150 mL) in a rotating 2-L flask. The pressure in the reactor was kept at 75 × 10^{-5} Torr during the reaction. On evaporation of the Cr, the soln turned an intense red-brown color. At the end of the reaction the power supply to the electrodes was cut and, after 10 min, the cooling bath was removed. Volatiles were distilled into a cold trap under vacuum. The flask was then removed under an atmosphere of argon. Excess naphthalene was sublimed onto a liq N_2 cooled cold finger (1 h, 40 °C, 75 × 10^{-5} Torr) and the black residue was extracted with N_2-sat. toluene (3 × 100 mL). After filtration under N_2 over Celite and concentration, the soln was diluted with pentane and then placed on dry ice. Black crystals of the highly air-sensitive product were isolated by decantation and washed with pentane; yield: 2.49 g (43%); ^{1}H NMR (benzene-d_6, δ):[15] 4.37 (m, 2H), 5.28 (m, 2H), 6.90 (m, 2H), 6.92 (m, 2H).

2.4.2 Method 2: Synthesis of Metal–Bis(arene) Complexes by Reductive Methods

The earliest synthesis of bis(benzene)chromium(0) (**1**, M = Cr; R¹ = H) and mixed benzene/biphenyl analogues goes back to 1919, when Hein treated anhydrous chromium(III) chloride in diethyl ether with phenylmagnesium bromide. It was only in 1954, however, that these compounds were recognized as being π-complexes. A mild reductive methodology is of preparative value for the naphthalene complexes. The chromium and molybdenum complexes **2** (M = Cr, Mo) as well as methyl-substituted derivatives are obtained by potassium evaporation into a solution of molybdenum or chromium halides and naphthalene in tetrahydrofuran.[19] Alternatively, the sandwich complexes are obtained by reaction of molybdenum(V) chloride or bis(tetrahydrofuran)molybdenum(IV) chloride and the arene with a highly reactive slurry of magnesium in tetrahydrofuran.[16] The involvement of arene radical anions in these reactions is probable. Indeed, as shown by Ellis and co-workers, naphthalene sandwich complexes **2** (M = Cr, Mo) are accessible in 20–25% yield via reaction of alkali metal naphthalenides with tris(tetrahydrofuran)chromium(III) chloride, tris(tetrahydrofuran)molybdenum(III) chloride, or bis(tetrahydrofuran)molybdenum(IV) chloride.[20]

For benzene and its methylated derivatives, the bis(arene)metal complexes of chromium, molybdenum, and tungsten (e.g., **1**, M = Cr, Mo, W; R¹ = H, Me) have been synthesized by heating a metal halide with aluminum powder in the presence of aluminum trichloride and the arene (Fischer–Hafner synthesis; Scheme 2). The method is limited to simple arenes that are not themselves reactive under Friedel–Crafts conditions. The initially formed cationic complexes $[M(arene)_2][AlCl_4]$ are readily reduced to the neutral 18-electron compounds by aqueous dithionite (for chromium) or by alkaline disproportionation with hydroxide (for molybdenum and tungsten). Conversely, the neutral complexes are readily oxidized to the cations. For a given arene, yields in the Fischer–Hafner synthesis decrease in the order Cr > Mo >> W. The complexes **1** (M = Cr, Mo, W; R¹ = H) thus are obtained in 95% yield for the chromium complex,[21] 71% for the molybdenum complex,[22] and 2% for the tungsten complex.[22] A modified one-pot procedure involving reduction of chromium and molybdenum chlorides with aluminum/aluminum trichloride in refluxing toluene followed by treatment with tetrahydrofuran affords the chromium sandwich complex **1** (M = Cr; R¹ = Me) in quantitative yield and the molybdenum analogue in 40% yield.[23] Another modification uses triethylaluminum as the reducing agent in place of aluminum/aluminum trichloride.[24]

Scheme 2 Metal–Bis(arene) Complexes Prepared by the Fischer–Hafner Method[21,22]



R¹ = H, Me

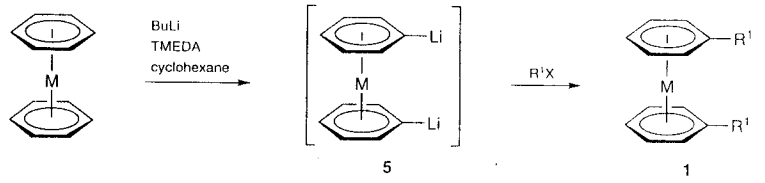
Bis(η^6-benzene)molybdenum(0) (1, M = Mo; R^1 = H); Typical Procedure:[25]
All operations have to be carried out in a dry, inert atmosphere using Schlenk techniques. Intermediates may be handled briefly in air, but [Mo(η^6-C_6H_6)$_2$] is immediately decomposed by oxygen. $MoCl_5$ (65 g, 238 mmol), anhyd $AlCl_3$ (140 g, 1050 mmol), and Al powder (8.5 g, 315 mmol) were mixed in a 500-mL round-bottomed flask. Dry benzene (250 mL) (**CAUTION:** *carcinogen*) was added over a period of 15 min (exothermic reaction). After cooling to rt, the components were mixed by shaking and a reflux condenser was added. A Teflon sleeve was used on the flask joint to prevent it from freezing. The reflux condenser was tightly wired to the flask, and the apparatus was connected to a N_2 line containing a Hg bubbler with a sufficient Hg level to give an excess pressure of 775–880 Torr. A safety shield was placed in front of the apparatus, the N_2 pressure was increased until a slow stream of bubbles was emitted from the Hg bubbler, and the temperature was slowly raised to 120 °C. After 12 h at reflux, the apparatus was cooled to rt, and the contents were mixed by shaking. The reflux was then continued for another 12 h. After cooling to rt, as much as possible of the benzene soln was decanted. The residue was washed with hexane (4 × 250 mL) and dried under vacuum. A 3-L, three-necked flask was equipped with a magnetic stirring bar and a N_2 inlet. Aq KOH (750 g in 1750 mL H_2O) was added and purged from air by bubbling N_2 for 10 min. The soln was cooled to −15 °C and the dried solid obtained before was added in small portions over about 2 h, under a strong N_2 countercurrent (the temperature was kept below −5 °C). After the addition was complete, the mixture was warmed slowly to rt and stirred for another 2 h. The contents of the flask were then filtered on a glass filter with a Celite plug, the solid was washed with H_2O (250 mL), and dried under vacuum. (**CAUTION:** *The dry solid is highly pyrophoric.*) The solid was finely pulverized and extracted with hot benzene (1 L in total). The hot benzene soln was filtered, the green filtrate concentrated to 150 mL, and cooled to 6 °C for 1 h. The bright green solid was removed by filtration, washed with petroleum ether (100 mL), and dried under vacuum; yield: 17.3 g (34.5%).

2.4.3 Method 3: Synthesis of Metal–Bis(arene) Complexes by Arene Exchange, by Arene Transformation Reactions, and by Cyclic Condensation Reactions

Reversible arene exchange occurs in [Cr(arene)$_2$]$^+$ complexes in the presence of aluminum trihalides.[26] The zero-valent chromium sandwich complexes are generally inert to thermal arene exchange.[27] An exception is bis(naphthalene)chromium(0) (**2**, M = Cr), which exchanges one naphthalene ligand for another arene at temperatures of 80 °C (in the presence of tetrahydrofuran) or 150 °C (in the neat arene) to give the mixed sandwich complexes.[27] Both arene ligands in bis(η^6-benzene)molybdenum(0) are exchanged when heated under vacuum in a sealed tube at 160 °C for two days in neat alkylbenzene (alkyl = Et, iPr, *t*-Bu). Yields are 60–70%.[367]

Arene transformations in metal–bis(arene) complexes have been much less studied than analogous reactions with (arene)tricarbonylchromium complexes (*vide infra*), largely because of the more difficult synthesis and handling of the sandwich compounds compared to the tricarbonyl complexes. Lithiation of bis(η^6-benzene)chromium(0) with butyllithium and tetramethylethylenediamine in cyclohexane gives predominantly the dilithiated complex **5** (M = Cr), which can be trapped with electrophiles to give the disubstituted derivatives **1** (M = Cr; R^1 = SMe[220], COPh[385], $SiPh_3$[386], SeMe[28]) (Scheme 3).[28] Similar reactions also occur with the molybdenum analogue of **5**, obtained by chlorine–lithium exchange from complex **1** (M = Mo; R^1 = Cl).[29] The naphthalene complex **2** (M = Cr) reacts with but-2-yne at ambient temperature to give bis(hexamethylbenzene)chromium(0).[27] This complex is also obtained in modest yield in cyclotrimerization reactions of but-2-yne with triphenyltris(tetrahydrofuran)chromium(0).[30]

Scheme 3 Lithiation–Electrophilic Addition Reactions with Metal–Bis(arene) Complexes[28]



5 1

Bis[η^6-(methylsulfanyl)benzene]chromium(0) (1, M = Cr; R^1 = SMe):[220]
All manipulations have to be carried out under an inert atmosphere and with dry solvents. [Cr(η^6-C_6H_6)$_2$] (1.5 g, 7.2 mmol) in cyclohexane (100 mL) was stirred during 15 h at rt with 2.2 M BuLi in hexane (6.47 mL, 14.37 mmol) and TMEDA (2.16 mL). A soln of MeSSMe (1.27 mL, 14.2 mmol) in toluene (40 mL) was then added to the red-brown mixture at −5 °C over 10 min. After the end of the addition, the resulting yellow-brown soln was stirred for 1 h at rt, filtered over alumina/8% H_2O, and the solvents were evaporated to dryness. The mixture obtained was fractionated by chromatography on alumina/8% H_2O in a pipe made of polyamide sheet (70 cm, diameter 2.5 cm) with petroleum ether (bp 40/60 °C) as eluent. When the three bands were separated (starting material > monosubstituted product > disubstituted product) the column was dried and the last band collected under exclusion of air. Recovery of the product by THF extraction and recrystallization (petroleum ether) afforded the product; yield: 1.26 g (58%); ^{1}H NMR (benzene-d_6, δ): 2.08 (s, 6H), 4.24 (dd, 2H), 4.28 (td, 4H), 4.71 (dddd, 4H).

2.4.4 Method 4: Synthesis of Tricarbonylmetal–Arene Complexes from Metal–Carbonyls

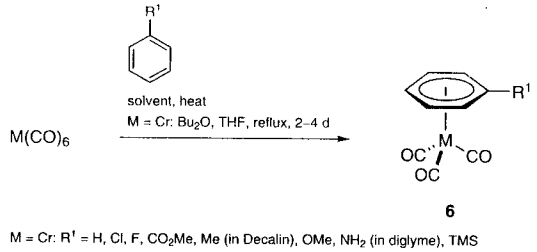
The (arene)tricarbonyl complexes of chromium, molybdenum, and tungsten are yellow to red, often crystalline compounds, which are stable to air in the solid state and can be stored for long periods, provided that they are kept out of light. In solution, they are moderately (chromium, tungsten) to strongly (molybdenum) air sensitive.

2.4.4.1 Variation 1: From Hexacarbonylmetal Complexes

The preferred method for the synthesis of (arene)tricarbonylchromium(0) complexes **6** (M = Cr) is thermolysis of hexacarbonylchromium(0) under an inert atmosphere (nitrogen or argon) in the presence of an excess of the arene, in a high-boiling solvent (Scheme 4). This can be the arene itself, dibutyl ether/tetrahydrofuran,[31] 1,2-dimethoxyethane,[32] diglyme/tetrahydrofuran,[33] heptane/diglyme,[34] α-picoline,[35] Decalin/ethyl formate, or Decalin/butyl acetate.[36,37] For aryl amino acids, a mixture of water and tetrahydrofuran (80:20) has been successfully applied.[38] The polar ether and ester additives (or solvents) promote carbonyl dissociation, stabilize intermediates, and the vigorous reflux of lower boiling additives washes sublimed hexacarbonylchromium(0) back into the reaction. The most widely used solvent combination is dibutyl ether/tetrahydrofuran (9:1).[31] This allows the preparation of a wide range of complexes in good yields with reaction times typically in the 1–4 day range. Higher temperatures shorten the reaction times but increase the risk of decomposition, which, once started, can lead to rapid product loss. Special apparatus (double condenser system[36] or distillative recycling of hexacarbonylchromium[39]) is advantageous or required in some of the procedures. Complexes of condensed aromatics are unstable toward polar solvents (tetrahydrofuran, dimethyl sulfoxide, acetone) and their synthesis requires special care[40–42] or the use of more labile [Cr(CO)$_3$L$_3$]

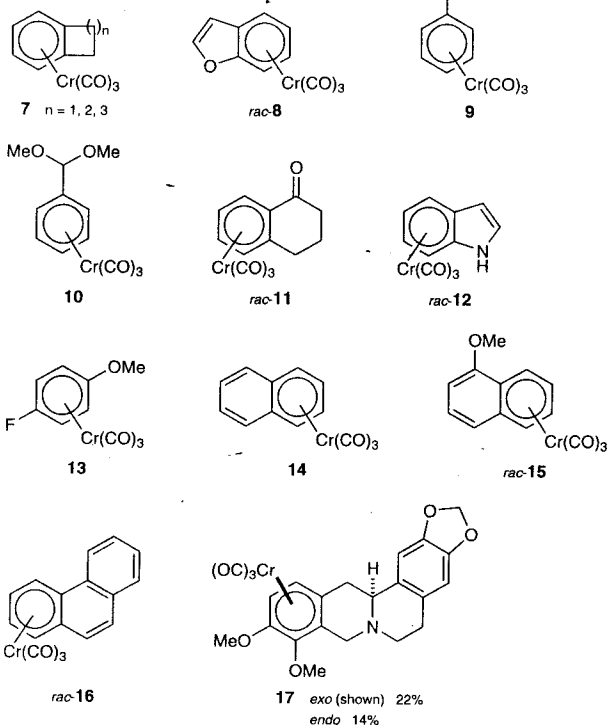
precursors (*vide infra*). A selection (**7**–**17**) from the hundreds of mono- and polysubstituted chromium–arene complexes made by this method is shown in Scheme 4. Condensed aromatics coordinate the metal in a terminal ring (e.g., in the phenanthrene complex **16**). This can be attributed to a minimum disruption of aromaticity.[43] Regioselectivity favors the arene over the heteroarene ring (e.g., in the indole complex **12**) and the nonsubstituted arene ring in 1-mono- and 1,4-disubstituted naphthalenes (e.g., in **15**).

Scheme 4 Synthesis of Tricarbonylmetal–Arene Complexes by Thermolysis of Hexacarbonylmetal Complexes



6

M = Cr: R^1 = H, Cl, F, CO_2Me, Me (in Decalin), OMe, NH_2 (in diglyme), TMS



Complex	Yield (%)	Ref	Complex	Yield (%)	Ref	Complex	Yield (%)	Ref
6 (M = Cr; R^1 = H)	89	[31]	**7** (n = 3)	85	[48]	**16**	27	[57]
6 (M = Cr; R^1 = Cl)	64	[31]	**8**	37	[54]	**6** (M = Mo; R^1 = H)	71	[46]
6 (M = Cr; R^1 = F)	90	[31]	**9**	83	[51]	**6** (M = Mo; R^1 = H)	95	[45]
6 (M = Cr; R^1 = CO_2Me)	89	[31]	**10**	86	[52]	**6** (M = Mo; R^1 = Me)	96	[45]
6 (M = Cr; R^1 = Me)	80	[48]	**11**	78	[53]	**6** (M = Mo; R^1 = NMe_2)	35	[58]
6 (M = Cr; R^1 = OMe)	85	[31]	**12**	80	[54]	**6** (M = Mo; R^1 = $SnMe_3$)	75	[59]
6 (M = Cr; R^1 = NH_2)	89	[48]	**13**	61	[55]	**6** (M = W; R^1 = H)	20	[60]
6 (M = Cr; R^1 = TMS)	96	[49]	**14**	70	[44]	**6** (M = W; R^1 = H)	80	[46]
7 (n = 1)	40	[50]	**14**	65–90	[41]	**6** (M = W; R^1 = Me)	31	[60]
7 (n = 1)	73	[27]	**14**	50–75	[42,51]	**6** (M = W; R^1 = NMe_2)	82	[60]
7 (n = 2)	78	[50]	**15**	77	[56]	**17**	36	[61]

Direct synthesis of [M(CO)$_3$(arene)] complexes **6** (M = Mo, W; R^1 = H, Me, NMe_2, $SnMe_3$) from an arene and [M(CO)$_6$] complexes is much more limited than for chromium.[44,45] The long reaction times at elevated temperature and the high sensitivity to oxygen often results in low yields for substituted arenes. A more useful procedure in these cases is arene exchange (for molybdenum) or ligand substitution in [M(CO)$_3$L$_3$] complexes (see Sections 2.4.4.2 and 2.4.4.3). (Benzene)tricarbonylmolybdenum(0) has been obtained in near quantitative yield.[45] The long reaction time (10 days) can be shortened by reacting hexacarbonylmolybdenum(0) in benzene in the presence of pyridine in an autoclave.[46] For the tungsten analogue, ammonium tetrafluoroborate is a better initiator than pyridine.[46] (Arene)tricarbonylchromium(0) complexes have also been prepared in low to moderate yields by photolysis of hexacarbonylchromium(0) in the presence of the arene.[47]

(η^6-Anisole)tricarbonylchromium(0) (6, M = Cr; R^1 = OMe):[31]

A 500-mL, round-bottomed flask fitted with a wide, straight-bore water-cooled condenser of 30-cm length was charged with Cr(CO)$_6$ (7.50 g, 34 mmol), anisole (7.35 g, 68 mmol), and Bu_2O (150 mL). The mixture was subjected to three freeze–pump–thaw cycles. Freshly distilled, dry, N_2-sat. THF (10 mL) was added next and the magnetically stirred mixture was heated at reflux in the dark under N_2 for 60 h. [The original procedure used 1 equiv of anisole. A better yield was obtained by the authors on using 2 equiv and on increased reaction time; this also allowed avoiding the separation of unreacted Cr(CO)$_6$.] After cooling to rt, the volatiles were distilled off on a rotary evaporator with a water bath held at 60 °C (an oil pump may be required to remove the solvent completely). The yellow residue was dissolved in dry, degassed Et_2O and filtered over Celite under a N_2 atmosphere. Crystallization (Et_2O/hexane) gave the yellow crystalline product; yield: 7.81 g (94%); mp 84–85 °C (Et_2O/hexane); IR (cyclohexane) $\tilde{\nu}_{CO}$: 1980, 1908 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 3.60 (s, 3H), 4.77 (t, 1H), 5.03 (d, 2H), 5.40 (t, 2H).

Tricarbonyl(η^6-naphthalene)chromium(0) (14):[42]

In a 500-mL, round-bottomed flask equipped with a two-stage condenser were placed naphthalene (25 g, 195 mmol), Cr(CO)$_6$ (10 g, 45 mmol), ethyl formate (20 mL), and Decalin (350 mL). The mixture was degassed three times and heated in the dark under N_2 to 240 °C for 6 h. [In the two-stage condenser, the lower stage is cooled by acetone (reflux). Naphthalene and Cr(CO)$_6$ sublime to this level. The upper stage is cooled by water (solvents condense here and then wash down the sublimed solids).] The mixture was then cooled to 60 °C, filtered on Celite under N_2, diluted with dry hexane (300 mL), and left at –30 °C over-

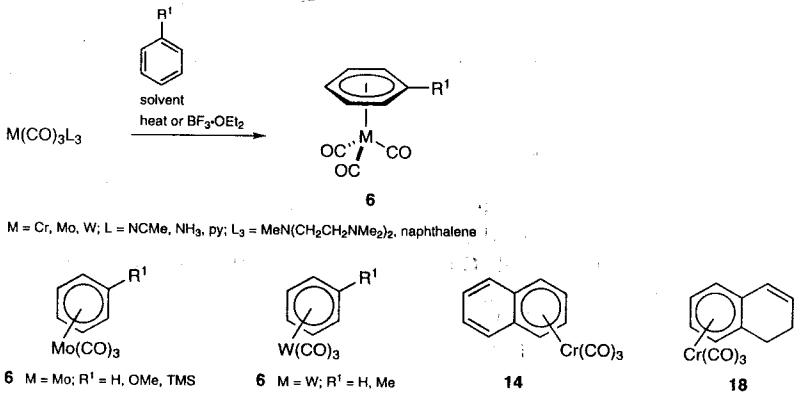
night. The solid obtained was isolated by decantation and dried under vacuum. Sublimation of excess naphthalene gave the product as a red crystalline solid; yield: 8.30 g (70%) [The literature method, carried out with technical grade $Cr(CO)_6$, reportedly gave a yield of 50%.[42] Pure $Cr(CO)_6$ and rigorous degassing routinely give yields in the 65–75% range.]; ^{1}H NMR (benzene-d_6, δ): 4.58–4.64 (m, 2H), 5.21–5.28 (m, 2H), 6.70–6.76 (m, 2H), 6.83–6.90 (m, 2H).

2.4.4.2 Variation 2: From $[M(CO)_3L_3]$ Complexes

Milder complexation conditions and shorter reaction times are possible with suitable $[M(CO)_3L_3]$ precursors (Scheme 5). For chromium, these include the complexes with L = acetonitrile, ammonia, or pyridine. $[M(NCR)_3(CO)_3]$ and $[M(CO)_3(pyridine)_3]$ are prepared by heating $[M(CO)_6]$ in the appropriate solvent under reflux. Reaction times increase from chromium to tungsten. With molybdenum, and particularly with tungsten, it is better to use the higher boiling propionitrile rather than acetonitrile. Tris(ammine)tricarbonylchromium(0) is best prepared by treating hexacarbonylchromium(0) with potassium hydroxide in ethanol, followed by addition of ammonium hydroxide (90% yield on a 10 g scale).[62,63] (Arene)tricarbonylchromium complexes are obtained on heating at reflux the pyridine and ammonia precursor complexes in the presence of an arene in dioxane. Room temperature complexation of arenes is accomplished by reaction of tris(ammine)tricarbonylchromium(0) or $[M(CO)_3(pyridine)_3]$ with boron trifluoride–diethyl ether complex in the presence of an arene[64] or heteroarene (see Section 2.4.9). Other sources of $[M(CO)_3]$ fragments are $[W(CO)_3\{MeN(CH_2CH_2NMe_2)_2\}]$ with boron trifluoride-diethyl ether complex,[65] $[Mo(CO)_3(diglyme)]$,[66] and $[Mo(CO)_3(DMF)_3]$.[67]

The advantages of lower temperatures for arene complexation are higher compatibility with arenes bearing functional groups and higher chemo- and diastereoselectivities (see also Sections 2.4.4.3, 2.4.7.2, and 2.4.9).[68] For example, heating the protected 1-oxobenzocyclobutene with tris(ammine)tricarbonylchromium(0) affords complex **19** in 83% yield (the unprotected compound cannot be complexed) (Scheme 5).[69] A very mild and high-yielding procedure for the synthesis of the naphthalene complex **14** consists of treating tris(ammine)tricarbonylchromium(0) with boron trifluoride–diethyl ether complex in the presence of the arene (dichloromethane, room temperature, 5 days, 90%).[70] While these methods require an additional synthetic step to prepare the $[M(CO)_3L_3]$ complexes, the ease of the procedures and the high overall yield make them often the methods of choice.

Scheme 5 Synthesis of $[M(CO)_3(arene)]$ Complexes from Labile Precursors[27,63,64,70–74]



Precursor	Product	Yield (%)	Ref
$Mo(CO)_3(pyridine)_3 + BF_3•OEt_2$	**6** (M = Mo; R^1 = H)	65	[64]
$Mo(CO)_3(pyridine)_3 + BF_3•OEt_2$	**6** (M = Mo; R^1 = OMe)	58	[64]
$W(CO)_3(MeNCH_2CH_2NMe_2)_2 + BF_3•OEt_2$	**6** (M = W; R^1 = H)	27	[65]
$W(CO)_3(MeNCH_2CH_2NMe_2)_2 + BF_3•OEt_2$	**6** (M = W; R^1 = Me)	56	[65]
$Cr(CO)_3(NH_3)_3 + BF_3•OEt_2$	**14**	70	[70]
$Cr(CO)_3(NH_3)_3$, dioxane, heat	**18**	85	[63]
$Cr(CO)_3(NH_3)_3$, dioxane, heat	**19**	83	[69]
$Cr(CO)_3(NCMe)_3$	**20**	35	[72]
$Cr(CO)_3(C_{10}H_8)$ (**14**)	**20**	90	[27]
$Cr(CO)_6$	**21**	92 [(*endo*/*exo*) 65:35]	[73]
$Cr(CO)_3(C_{10}H_8)$ (**14**)	**21**	87 [(*endo*/*exo*) 90:10]	[73]
$Cr(CO)_3(C_{10}H_8)$ (**14**)	**22**	97 (1 diastereomer)	[74]

Tricarbonyl(η⁶-1,2-dihydronaphthalene)chromium(0) (18):[63]
In the dark and under N_2, a magnetically stirred mixture of 1,2-dihydronaphthalene (2.60 g, 20 mmol) and $[Cr(CO)_3(NH_3)_3]$ (4.87 g, 26 mmol, 1.3 equiv) in anhyd dioxane (250 mL, deoxygenated and peroxide-free) was heated at reflux for 6 h. Removal of volatiles under vacuum and crystallization (hexane/Et_2O 4:1) afforded the product; yield: 4.52 g (85%); mp 108 °C; IR (KBr) $\tilde{\nu}_{CO}$: 1950, 1860, 1830 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.50 (m, 4H), 5.20 (m, 4H), 6.05 (m, 2H).

2.4.4.3 Variation 3: By Arene and Heteroarene Exchange

Arene exchange reactions in (arene)tricarbonylmetal complexes are equilibrium reactions, and a large excess of the incoming arene may be required to drive the reaction to the product. Equilibria are reached faster in the presence of coordinating solvents. For chromium, elevated temperatures are required for exchange (>140 °C in tetrahydrofuran)[75] and concomitant decomposition of complexes under these conditions is a problem for all but simple alkylarenes. For this reason, arene exchange in $[Cr(CO)_3(arene)]$ complexes is not a useful synthetic method except for labile complexes such as tricarbonyl(naphthalene)chromium(0) (**14**).[27] Complex **14** and other tricarbonylchromium complexes of fused aromatics undergo intramolecular haptotropic rearrangements on heating to ca. 100 °C.[76–79] Theoretical analysis for the degenerate rearrangement of **14** favors a reaction pathway via an exocyclic intermediate.[80] In the absence of a Lewis basic solvent, arene exchange in **14** is about 20 times slower than the intramolecular rearrangement. However, Lewis basic solvents considerably accelerate arene exchange. In tetrahy-

drofuran it occurs slowly already at ambient temperature, and rapidly on heating to 80 °C. The mechanism involves haptotropic slippage of the naphthalene ligand (change from η^6- to η^4- or η^2-coordination), thus facilitating the dissociation and coordination of the new arene.[81] The mild conditions are particularly suited for diastereoselective complexation reactions (see Section 2.4.7.2). A variant is the in situ generation of the naphthalene complex under conditions of arene exchange.[82] Facile arene exchange also occurs with tricarbonyl(1-methylpyrrole)chromium(0) (see Section 2.4.9).[83] This has not found widespread application yet because this complex is not easy to handle (it is pyrophoric and is best handled under an inert atmosphere in a glove box). Mild arene exchange also occurs upon generation of a benzylic cation (see Section 2.4.6.2),[84] or catalyzed by iodine (the reaction presumably passes via formation of a labile 17-electron complex).[85] This has not been used much but may have considerable potential. Finally, an unusual synthesis of tricarbonyl(styrene)chromium(0) (**20**) consists of co-condensing chromium atoms (see Section 2.4.1) with styrene at −196 °C followed by warm up under a carbon monoxide atmosphere.[86] With reference to the stepwise displacement of naphthalene in bis(naphthalene)chromium(0) (**2**, M = Cr) by carbon monoxide,[14] the intermediacy of the styrene sandwich complex is likely.

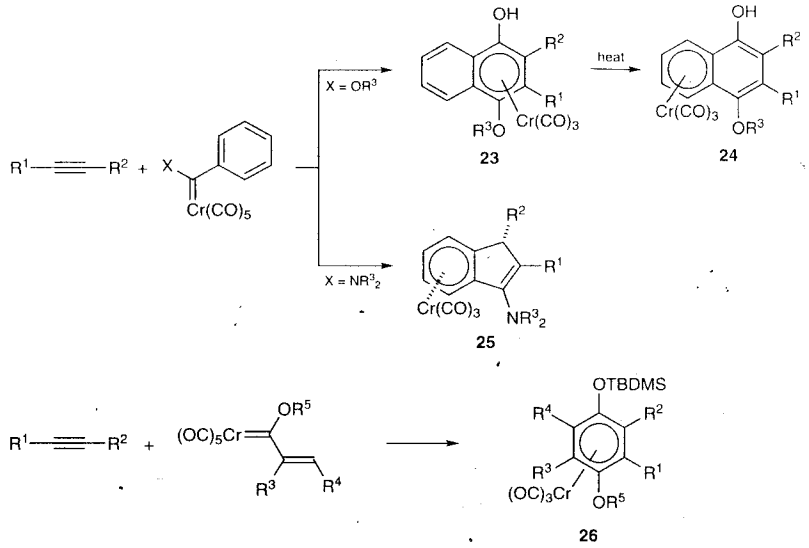
The more labile (arene)tricarbonylmolybdenum complexes undergo arene exchange readily and equilibria are reached rapidly when (benzene)tricarbonylmolybdenum(0) (**6**, M = Mo; R^1 = H) is reacted with arenes (anisole, trimethylsilylbenzene) in the presence of tetrahydrofuran.[87]

Tricarbonyl(η^6-trimethylsilylbenzene)molybdenum(0) (6, M = Mo; R^1 = TMS):[87]
$[Mo(CO)_3(\eta^6\text{-}C_6H_6)]$ (1.20 g, 4.7 mmol) was suspended in PhTMS (2.66 g, 17.7 mmol) and THF (4 mL) was added. After stirring for 5 h at rt, all volatiles were removed under vacuum. The residue was dissolved in warm hexane and filtered through Avicel. Cooling to −30 °C overnight afforded the product as fine yellow crystals; yield: 1.48 g (97%); IR (hexane) $\tilde{\nu}_{CO}$: 1981, 1947, 1911 cm^{-1}; ^1H NMR (benzene-d_6, δ): 0.06 (s, 9H), 4.56–4.60 (m, 2H), 4.88 (t, 1H), 4.97 (d, 2H).

2.4.4 Variation 4: From (Carbene)pentacarbonylmetal Complexes

The reaction of chromium carbene complexes with alkynes to give naphthol derivatives (Dötz annulation) has been extensively studied (Scheme 6).[88–91] A dissociative mechanism has been proposed, involving the loss of one carbonyl ligand followed by alkyne coordination, carbene insertion, carbonyl insertion, electrocyclization, and finally tautomerization to the naphthol skeleton. The carbene carbon preferentially couples to the alkyne carbon bearing the smaller substituent. On heating, the initially formed naphthol complex **23** undergoes haptotropic rearrangement to the isomer **24**, containing the tricarbonylchromium fragment coordinated to the unsubstituted naphthalene ring. If an aminocarbene is used, carbonyl insertion does not take place and **25** is the sole product. In some cases an oxycarbene can also lead to the five-membered ring, and product selectivity can be controlled to some extent by variations on carbene structure, solvent, temperature, and concentration. Vinylcarbene complexes react analogously, producing phenol derivatives such as **26**. Although the primary products of these annulation reactions are η^6-arene complexes, these are often not isolated but directly treated with iodine or exposed to air and sunlight to remove the metal. In order to isolate the chromium complex with good yields, it is usually necessary to protect the phenol or naphthol function formed in the reaction.[92]

Scheme 6 Dötz Annulation[88–91]



Arene chromium complexes obtained by Dötz annulation are chiral. For examples of diastereoselective versions of this reaction, see Section 2.4.7.5.

Tricarbonyl[η^6-1-methoxy-5-propyl-4-(tributyldimethylsiloxy)-2-(trimethylsilyl)benzene]chromium(0) (26, R^1 = R^4 = H; R^2 = Pr; R^3 = TMS; R^5 = Me); General Procedure:[92]
The carbene complex (typically 0.5–5.0 mmol, 1.0 equiv) was placed in a modified flask (a single-neck, pear-shaped flask that has been modified by replacement of the 14/20 joint with a 10-mm threaded high-vacuum stopcock), the stopcock was replaced with a rubber septum, and the flask was evacuated and backfilled with argon. One half of the volume of anhyd CH_2Cl_2 required for a 0.05 M soln of the carbene complex, the alkyne (1.5 equiv), anhyd 2,6-lutidine (2.5 equiv), TBSOTf (1.5 equiv), and the remaining solvent were added by syringe. Under a stream of argon, the septum was replaced quickly with the threaded stopcock, the soln was degassed using the freeze–pump–thaw method (three cycles), and the flask backfilled with argon. After heating at 50 °C until the carbene complex was consumed (12–24 h), the mixture was diluted in Et_2O, washed once with H_2O, twice with dil HCl, once with brine, and dried ($MgSO_4$). Following filtration and removal of volatiles at reduced pressure, the arene complex was purified by flash chromatography on silica gel; yield: 79%; yellow solid; mp 77–79 °C; IR (neat) $\tilde{\nu}_{max}$: 1953, 1871, 1466, 1343, 1253, 1203, 1000 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.32 (s, 12H), 0.33 (s, 3H), 0.97 (s, 9H), 1.05 (t, 3H), 1.56–1.62 (m, 1H), 1.63–1.73 (m, 1H), 2.14–2.20 (m, 1H), 2.83–2.89 (m, 1H), 3.77 (s, 3H), 4.95 (s, 1H), 5.31 (s, 1H).

Similarly prepared was tricarbonyl[η^6-1-methoxy-2-methyl-5-propyl-4-(tributyldimethylsiloxy)benzene]chromium(0) (**26**, R^1 = R^4 = H; R^2 = Pr; R^3 = R^5 = Me); yield: 77%; yellow solid; mp 76–78 °C; IR (neat) $\tilde{\nu}_{max}$: 1952, 1865, 1482, 1370, 1233, 1210, 1019 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.30 (s, 3H), 0.38 (s, 3H), 0.99 (s, 9H), 1.02 (t, 3H), 1.55–1.65 (m, 2H), 2.13–2.18 (m, 1H), 2.15 (s, 3H), 2.65–2.70 (m, 1H), 3.70 (s, 3H), 5.13 (s, 1H), 5.25 (s, 1H).

2.4.5 Method 5: Synthesis of Tricarbonylmetal–Arene Complexes by Arene Modification

Coordination to a tricarbonylmetal group induces profound changes in the reactivity of the coordinated arene, both at the ring and at benzylic positions. To date, this has been

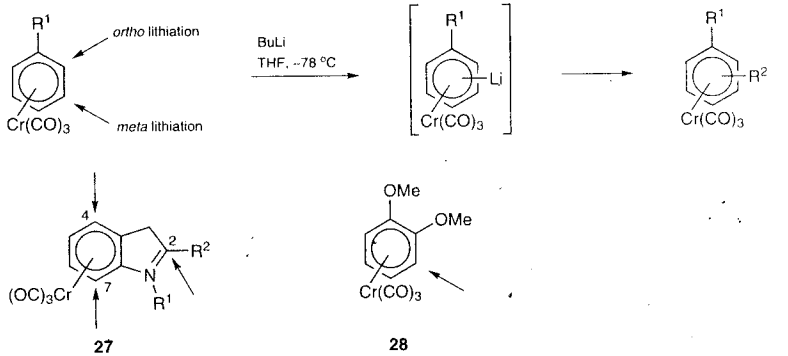
lemonstrated and used only in chromium complexes. The dominant feature of the tricarbonylchromium group is that of an electrophilic auxiliary. It inverses the reactivity of a complexed arene, renders the ring carbons susceptible to nucleophilic attack, and increases the acidity of ring and benzylic hydrogens. However, the tricarbonylchromium group also has donor properties and is capable of stabilizing a benzylic cation. This duality in function has led to widespread use of (arene)tricarbonylchromium complexes in organic synthesis. The steric blocking of one face of the arene by the tricarbonylchromium fragment, and the resulting control of stereochemistry, adds yet another powerful feature to these reactions. Transformations that result in new tricarbonylchromium–arene complexes are discussed below or, if they result in optically active complexes, in Section 2.4.7. Reactions that involve modifications of the arene side chain are presented in Section 2.4.6, and those that give products other than new (arene)tricarbonylchromium complexes will be discussed in Section 2.4.10.

2.4.5.1 Variation 1: Via Lithiation and Reaction with Electrophiles

Coordination of an arene to the electrophilic tricarbonylchromium fragment lowers the pK_a of ring protons by ca. 6 pK_a units compared to the free arene.[93,94] The first metalation of an arene chromium complex was reported in 1972,[95] and since then this reaction has seen extensive development and has been the subject of several reviews.[96–98]

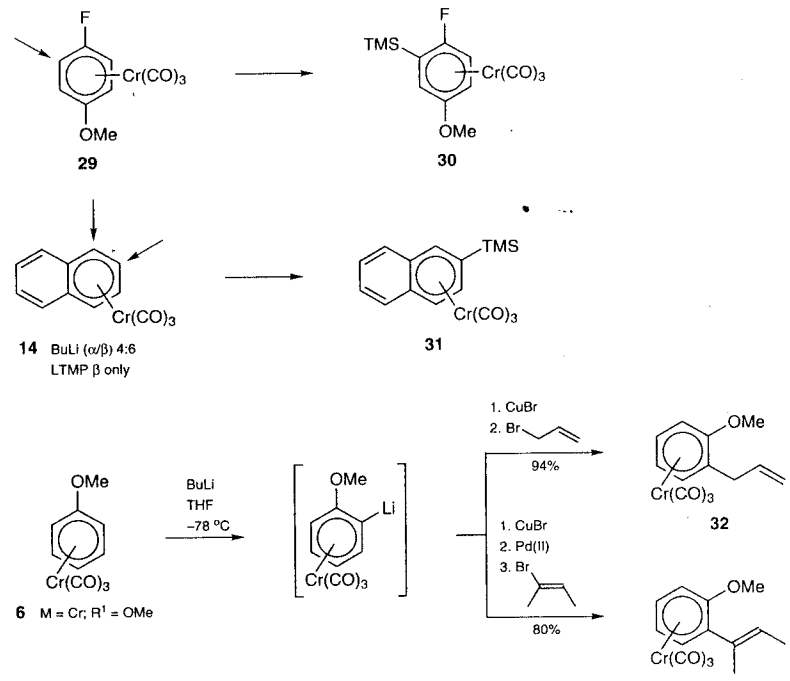
Deprotonation by reactive bases of low nucleophilicity such as lithium amides (lithium diisopropylamide, lithium 2,2,6,6-tetramethylpiperidide) gives $[Cr(CO)_3(Ar^1Li)]$ complexes that are usually reacted in situ with electrophiles. Depending on the nature of the reagent and the complex, alkyllithium reagents either react by deprotonation or by addition (see Section 2.4.5.2). Alternatively, though less often used, $[Cr(CO)_3(Ar^1Li)]$ complexes are accessible via lithium–halide exchange in $[Cr(CO)_3(Ar^1X)]$ (X = Br, I) complexes.[99] Double lithiation can be a problem in (anisole)tricarbonylchromium(0) (**6**, M = Cr; R^1 = OMe) and in tricarbonyl(veratrole)chromium(0) (**28**) (Scheme 7).[100] Complexes of alkylbenzenes generally react with low regioselectivity. Benzylic deprotonation is favored under thermodynamic conditions (potassium *tert*-butoxide, dimethyl sulfoxide, 25 °C),[101] but under kinetic conditions (butyllithium, tetrahydrofuran, −78 °C), deprotonation takes place preferentially, though generally not exclusively, at the ring. Thus, tricarbonyl(toluene)chromium(0) reacts with butyllithium at −78 °C at the benzylic site (20%) as well as at ring positions: 9% *ortho* and 35% each *meta* and *para*.[102] Examples of regioselectivity in deprotonation reactions under kinetic conditions are shown in Scheme 7. Bulky substituents readily block *ortho* substitution. Conversely, a number of functional groups direct metalation to the *ortho* position: F, Cl, OMe, OTMS, $OC(O)NR^1_2$, NMe_2, NHCO*t*-Bu, $CH(OMe)_2$, CH_2OMe, CH_2NMe_2, SOR^1. The *ortho* directing ability varies from that found in uncomplexed arenes and decreases in the order: F > NHCO*t*-Bu > OMe ≈ CH_2NMe_2 > CH_2OMe (e.g., for **29**).[55] Preferential *meta* lithiation occurs with OTIPS [(*m*/*p*) 9:1] and with NMe(TBDMS) [(*m*/*p*) 98:2] and this has been attributed to the preferred conformation of the "$Cr(CO)_3$" tripod at low temperature, with reaction occurring at a C_{Ar}—H eclipsed to a Cr—CO bond.[103] The cyclobutabenzene complex **7** (n = 1) is lithiated exclusively at the carbon alpha to the ring junction.[104,105] Increasing ring size in the benzocycloalkanes results in increasing deprotonation at the β-position [tricarbonyl(indane)chromium(0) (**7**, n = 2): (α/β) 1:2 (with butyllithium); 1:11 (with lithium 2,2,6,6-tetramethylpiperidide)].[104] The influence of the size of the base is also apparent in the deprotonation of the naphthalene complex **14**. Lithium 2,2,6,6-tetramethylpiperidide removes selectively H—C2, while butyllithium gives, after trapping with electrophiles, a 2:1 mixture of C2/C1 substituted products.[76–78] With complex **14**, deprotonation by lithium diisopropylamide has been shown to be reversible.[106] Deprotonation of N-protected indole complexes **27** is directed to the 2-, 4-, or 7-position, depending on the N-protecting group and the substituent at C2.[107] This is of synthetic significance since the 4-position in indoles is not readily attainable.

Scheme 7 Lithiation and Trapping with Electrophiles[55,76–78,99–102,106–109]



27 **28**

R^1	R^2	Position of Deprotonation of **27** Using BuLi	Ref
Me	H	2	[107]
$CH_2OCH_2CH_2TMS$	TMS	7	[107]
TIPS	H	4	[107]



Trapping of the in situ generated [$Cr(CO)_3(Ar^1Li)$] complex with reactive electrophiles [e.g., TMSCl, RSCl, PPh_2Cl, MoOPH, CO_2, RCHO, $ClCO_2Me$, $HCONMe_2$ (→ CHO), MeI] yields the substituted arene complexes.[96] The reaction with ketones to give benzyl alcohols can be inefficient because of competitive enolization. Allyl halides react cleanly only if metal exchange Li → Cu precedes the electrophile addition (e.g., to give **32**).[108] Transmetalation Li → Cu → Pd allows cross coupling with vinylic halides (e.g., to give **33**)[109] (see also Section 2.4.6.5). Multiple Lithiations (up to 3) occur when an excess of lithium diisopropylamide or lithium 2,2,6,6-tetramethylpiperidide is used. An electrophilic quench (e.g., with TMSCl) then affords di- or trisubstituted complexes {e.g., [η^6-1,3,5-tris(trimethylsilyl)benzene]tricarbonylchromium(0)}.[368]

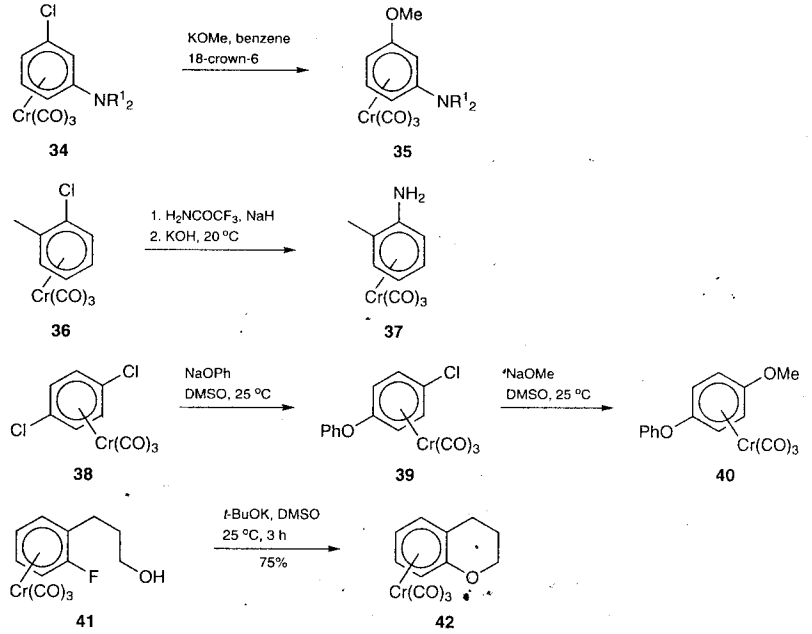
Tricarbonyl[η^6-4-fluoro-3-(trimethylsilyl)anisole]chromium(0) (30); Typical Procedure:[55]
[$Cr(CO)_3(\eta^6$-4-fluoroanisole)] (**29**; 214 mg, 0.82 mmol) was dissolved in THF (20 mL). After cooling to −78 °C, BuLi (1.0 equiv) was added and the resulting mixture stirred at this temperature for 45 min. An excess of TMSCl was added and the soln allowed to warm to rt overnight. The mixture was poured into 15% aq NH_4Cl/Et_2O, the organic portion was separated, washed (H_2O), dried, and the solvents were evaporated. After column chromatography (silica gel, petroleum ether/Et_2O 85:15), the product was isolated as yellow crystals; yield: 254 mg (93%); mp 69–70 °C; IR ($CHCl_3$) $\tilde{\nu}_{max}$: 1975, 1895, 1450, 1425 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.40 (s, 9H), 5.22 (t, 1H), 5.34 (dd, 1H), 5.45 (dt, 1H).

Tricarbonyl[η^6-2-(trimethylsilyl)naphthalene]chromium(0) (31):[78]
A soln of LTMP was prepared by addition of 1.6 M BuLi in hexane (0.52 mL, 1 mmol) to a cold (−78 °C) soln of TMP (0.17 mL, 1 mmol) in THF (3 mL). After 10 min, this soln was transferred to a double-jacketed dropping funnel maintained at −78 °C. The LTMP soln was then added dropwise, over a period of 10 min, to a cold (−78 °C) soln of [$Cr(CO)_3$(naphthalene)] (**14**; 264 mg, 1 mmol) in THF (7 mL). [Note: it is important to prepare the soln of the complex in cold THF (e.g., −20 °C) because of the lability of the naphthalene in **14** in the presence of Lewis bases.] During the addition, a color change from orange to deep red was observed. The soln was stirred a further 10 min at −78 °C and then TMSCl (0.125 mL, 1 mmol) was added in one portion. The mixture was stripped of volatiles during warming up and the resulting residue extracted with hexane. The soln was filtered through Celite and the filtrate concentrated in vacuo. Cooling to −78 °C produced orange crystals of the product; yield: 309 mg (92%); mp 132 °C; IR (hexane) $\tilde{\nu}_{max}$: 1977, 1917, 1900 cm^{-1}; ^1H NMR (benzene-d_6, δ): 0.30 (s, 9H), 5.11 (dd, 1H), 5.40 (d, 1H), 5.89 (s br, 1H), 6.90 (m, 2H), 7.03 (m, 2H).

2.4.5.2 Variation 2: Via Nucleophilic Substitution

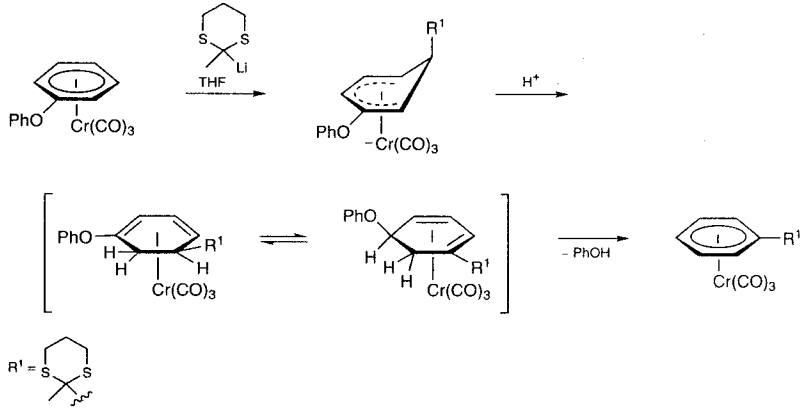
The electrophilic tricarbonylchromium group activates the arene ring toward nucleophilic attack. Chlorobenzene complexes readily undergo S_NAr substitution of chloride by hydroxide, alkoxide (e.g., **34** → **35**, **39** → **40**),[110] phenoxide (e.g., **38** → **39**),[111] and thiolate nucleophiles as well as by sodium hydride/trifluoroacetamide (e.g., **36** → **37**) (Scheme 8).[112] The reaction is particularly efficient under phase-transfer conditions, in benzene in the presence of crown ethers, or in dimethyl sulfoxide. In contrast, more reactive carbanions preferentially add *ortho* to the chlorobenzene complex **6** (M = Cr; R^1 = Cl) and *ipso* substitution is feasible only for nucleophiles that add reversibly. The fluoro complex **6** (M = Cr; R^1 = F) is even more reactive: in dimethyl sulfoxide, fluoride is substituted by a wide range of nucleophiles that include alkoxides, carboxylates, amines, and a variety of carbanions ranging from acetylides to ketone enolates.[113,114] An example of an intramolecular reaction is shown by the transformation **41** → **42**.[115]

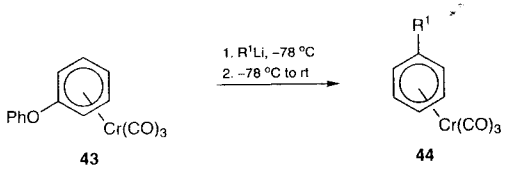
Scheme 8 *ipso* Nucleophilic Substitution[110–112,115]



An alternative sequence for an aromatic substitution of a halide, a phenoxide, or even a methoxide consists of a sequence of nucleophile addition, protonation, and elimination (Scheme 9).[116–118] Depending on the regioselectivity of nucleophile addition, the result of the sequence is a *cine* substitution (nucleophile addition *ortho* to the leaving group) or *tele* substitution (nucleophile addition *meta* or *para* to the leaving group) (e.g., **43** → **44**). Evidence for this mechanism stems from ^2H labeling of the starting complex. Yields of arene complexes can be low, because of competitive decomplexation of either the arene product or the rapidly interconverting, labile, agostic cyclohexadiene ligands.[119,120]

Scheme 9 *tele* Nucleophilic Substitution[116–118]



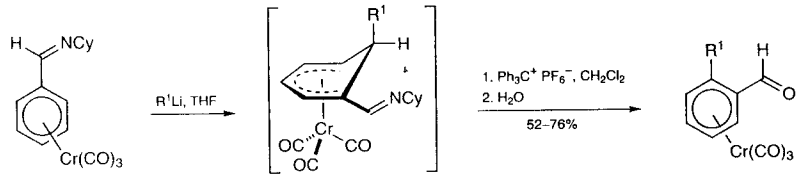


43 44

R¹ = CH_2CN, CH(Me)CN, CMe_2CN, CH(Me)CO_2t-Bu

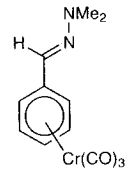
above methodologies have in common the requirement of a leaving group on the ne, since nucleophilic substitution of aromatic hydrogen is unfavorable. This has re-itly been realized, albeit in a stepwise fashion: *ortho* nucleophilic addition of organo-ium compounds to complex **45**, followed by an *endo* hydride abstraction, gives the *or*-substituted arene complexes **47** (Scheme 10).[121] The removal of the *endo*-hydride in **46** the trityl cation is thought to be facilitated by precoordination of the Lewis acid to the rogen lone pair. Complexes **9** and **48** react similarly. Diastereo- and enantioselective sions have been realized (see Section 2.4.7.4).

Scheme 10 Nucleophile Addition–Hydride Abstraction[121]



45 46 47

R¹ = Me, Bu, vinyl, Ph, thienyl, furyl



48

icarbonyl(η^6-2-phenylpropanenitrile)chromium(0) [44, R¹ = CH(Me)CN]:[116]

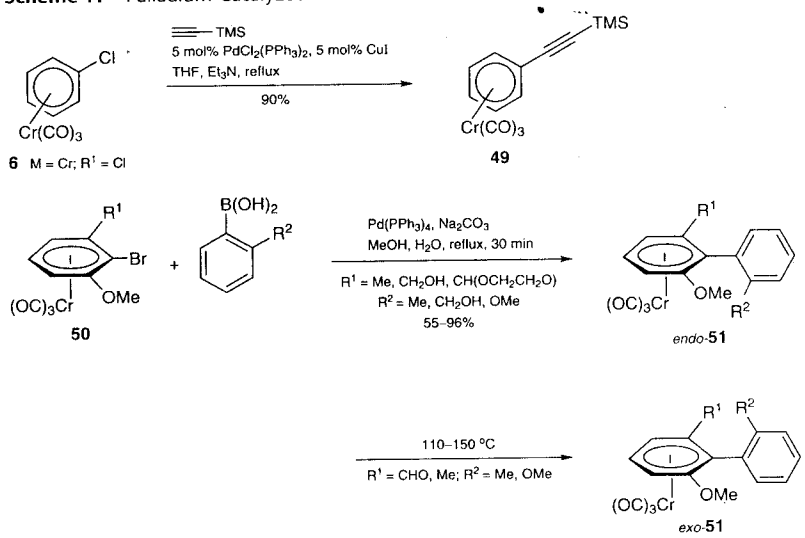
a soln of iPr_2NH (1.8 mL, 12.8 mmol) in THF (20 mL) at –78 °C was added 1.47 M BuLi in xane (8.2 mL, 12.1 mmol). The mixture was warmed to 0 °C for 20 min and then cooled ain to –78 °C. Propanenitrile (0.85 mL, 12.1 mmol) was added and, after 30 min, r(CO)$_3$(η^6-diphenyl ether)] (**43**; 3.06 g, 10 mmol) was added as a solid. After warming to overnight, the soln was extracted with Et_2O, washed with 5% aq HCl, 5% aq NaOH, and ine, and dried ($MgSO_4$). After evaporation of the solvents, the residue was purified by olumn chromatography (silica gel, petroleum ether/Et_2O 90:10 to 0:100), affording start-g material **43** (1.52 g, 50%) and the product **44**; yield: 1.13 g (42% after recrystallization acetone); IR ($CHCl_3$) $\tilde{\nu}_{max}$: 2250, 1980, 1900 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.6 (d, 3H), 3.6 (q, H), 5.3 (m, 5H).

4.5.3 Variation 3: Via Palladium-Catalyzed Reactions

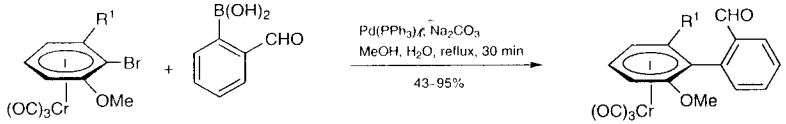
he complexation of a haloarene by a tricarbonylchromium group activates the C_{Ar}—X

um(0)/triphenylphosphine readily at ambient temperature and is 75 times more reactive than free bromobenzene.[122] We recall that with palladium(0)/triphenylphosphine, free chlorobenzene requires temperatures in excess of 130 °C, although this can be remedied by using the more basic bulky ligands tri-*tert*-butylphosphine.[123] The first report of a palladium-catalyzed reaction of **6** (M = Cr; R¹ = Cl) entailed a Sonogashira coupling with alkynes.[124] This reaction was subsequently modified and an example is shown in Scheme 11.[125] Another approach to (alkynylarene)tricarbonylchromium complexes involves a Stille cross-coupling reaction.[126] Palladium-catalyzed alkoxycarbonylation of **6** (M = Cr; R¹ = Cl) [25 °C, palladium(0)/triphenylphosphine, carbon monoxide, an alcohol], leading to complexed benzoic acid esters, was studied in detail and it was shown that "Cr(CO)$_3$" activation is important in the oxidative addition step (the insertion of Pd into the C_{Ar}—Cl bond).[122,127,128] With electron-poor arenes, *ipso* nucleophilic substitution is a competitive reaction.[129] Arylpalladium intermediates are also accessible via transmetalation (Li → Zn → Pd). This has been used successfully in the synthesis of moracin M, a phytoalexin of *Morus alba* Linn.,[130] and in the synthesis of aryl amino acid derivatives[131] (see also Section 2.4.5.1). Intramolecular Heck and related reactions of complexed *ortho*-alkenyl chloroarenes have been realized with excellent diastereocontrol of the stereogenic center formed in the alkene carbopalladation step.[132,133] Suzuki coupling reactions have been carried out with tricarbonyl(fluorobenzene)chromium(0).[134] Aryl—aryl bond formation via Suzuki coupling between (bromoarene)tricarbonylchromium(0) complexes and arylboronic acids has been studied in detail by Uemura and co-workers.[135,136] The finding that planar chiral complexes couple with substituted arylboronic acids with high diastereoselectivity has been developed into an efficient and elegant route to enantiopure atropisomeric biaryls with applications in natural product synthesis [e.g., (–)-steganone and *O,O'*-dimethylkorupensamine A; see also Section 2.4.11].[135] Diastereoselectivity is determined in the *cis*-biaryl palladium intermediate, and the kinetic product is the atropoisomer with the substituent *endo* to the "Cr(CO)$_3$" group (**50** → *endo*-**51**). On heating *endo*-**51** to 110–150 °C, isomerization to the thermodynamically favored *exo* isomer takes place. The *exo* diastereomer is formed directly under the reaction conditions with small R^2 substituents (e.g., CHO; **50** → **52**).[136]

Scheme 11 Palladium-Catalyzed Reactions[122,125,135,136]



6 M = Cr; R¹ = Cl 49 50 *endo*-51 *exo*-51



50 52

Tricarbonyl{η⁶-[(trimethylsilyl)ethynyl]benzene}chromium(0) (49); Typical Procedure:[125] Chlorobenzene complex **6** (M = Cr; R¹ = Cl; 3.73 g, 15.0 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.53 g, 0.74 mmol), and CuI (0.14 g, 0.74 mmol) were dissolved in THF (50 mL) and Et_3N (25 ml) under argon. A soln of TMSC≡CH (5.50 g, 22.4 mmol) in THF (50 mL) was added over 1 h at rt. The mixture was then heated at reflux for 6 h. After cooling to rt, Et_2O (50 mL) was added and the suspension filtered. The filtrate was evaporated and the residue purified by column chromatography (silica gel, Et_2O/pentane 1:12) to afford the product as yellow-orange crystals; yield: 4.20 g (90%); mp 74–75 °C; IR (KBr) $\tilde{\nu}_{max}$: 2150, 1944, 1869 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.08 (s, 9H), 5.00 (m, 1H), 5.15 (m, 2H), 5.26 (m, 2H).

2.4.6 Method 6: Synthesis of Tricarbonylmetal–Arene Complexes by Side-Chain Modification

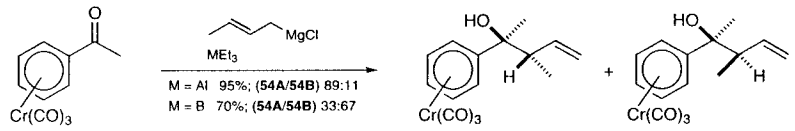
Side-chain functionalization in π-complexed arenes has been developed to date only in (arene)tricarbonylchromium complexes. The tricarbonylchromium fragment stabilizes both cationic and anionic benzylic intermediates;[137] being bulky, it also efficiently blocks one face of the arene and adjacent positions. All these effects have been used extensively.[138]

2.4.6.1 Variation 1: Via Nucleophile Addition

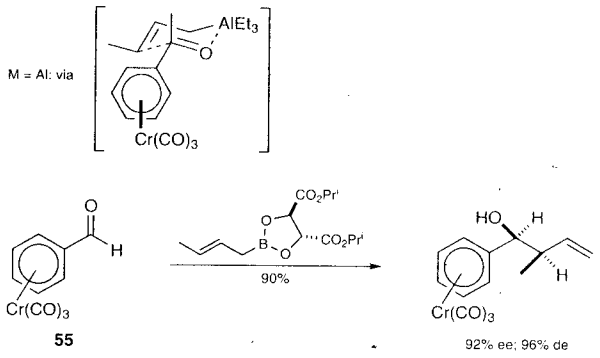
Tricarbonyl(styrene)chromium(0) (**20**) undergoes nucleophilic addition reactions [LiCMe₂CN, LiCMe(CN)OR] at the β-position to give a stabilized benzylic anion that can be trapped with reactive electrophiles (H^+, AcCl, MeI).[139] An analogous carbanion addition–protonation is also reported for tricarbonyl(dihydronaphthalene)chromium(0) (**18**) in a sequence directed toward anthraquinone synthesis (see Section 2.4.10).[140]

Crotylmagnesium chloride and Et_3M (M = B, Al) react with (alkyl phenyl ketone)tricarbonylchromium(0) (e.g., **53**) with allylic rearrangement to give preferentially the diastereomer **54A** when M = Al (cyclic transition state, "ate" complex; see Scheme 12) but the diastereomer **54B** when M = B (open transition state).[141] The same reaction (M = Al) with (benzaldehyde)tricarbonylchromium(0) (**55**) gives a 1:1 mixture of diastereomers. Enantioselective allylation of **55** with chiral allyl boronates affords the product with higher diastereoselectivity compared to the reaction with benzaldehyde itself.[142]

Scheme 12 Nucleophilic Addition to Ketone and Aldehyde Functions: Acyclic Substrates[141,142]



53 54A 54B

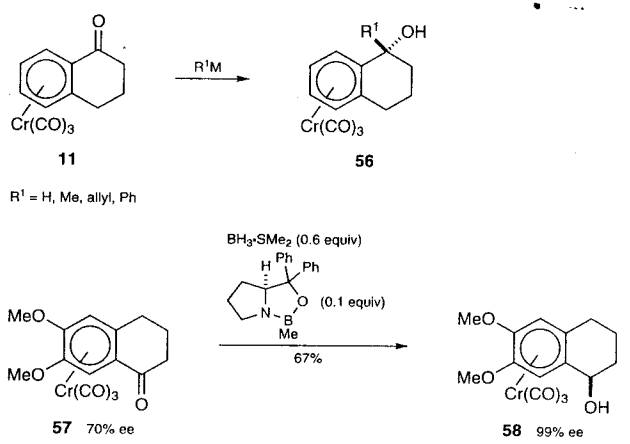


55 92% ee; 96% de

Nucleophilic addition to tricarbonylchromium complexes of aryl ketones and aldehydes occurs from the face opposite to the tricarbonylchromium group. This has stereochemical consequences if the carbonyl group is part of a ring structure {tetral-1-one [3,4-dihydronaphthalen-1(2*H*)-one], indan-1-one, etc.} or if it adopts a preferred conformation.

Tricarbonyl(tetral-1-one)chromium(0) (**11**) is accessible by direct complexation using hexacarbonylchromium(0)[53] or by oxidation of tricarbonyl(tetral-1-ol)chromium(0) (**56**, R¹ = H) [manganese(IV) oxide[144] or dimethyl sulfoxide/acetic anhydride[143]]. Complex **11** reacts with nucleophiles (lithium aluminum hydride, sodium borohydride, methyllithium, methylmagnesium bromide, allylmagnesium chloride, phenylmagnesium bromide) to give selectively the *endo*-alcohol products (e.g., **56**) (Scheme 13).[144–146] The indan-1-one complex[145,147] and the benzocyclobutanone complex[148,149] react analogously. Hydride addition (lithium aluminum hydride, sodium borohydride) to the tetral-2-one complex also gives the *endo*-alcohol as the major diastereomer (90–96% de).[96] An exception to the above is the borane reduction of tetralones catalyzed by chiral oxazaborolidines (CBS reduction). Here, catalyst stereocontrol overrides substrate stereocontrol and the tetralone complex **57** yields predominantly the *exo*-diastereomer **58** (Scheme 13).[150]

Scheme 13 Nucleophilic Addition to Ketone and Aldehyde Functions: Cyclic Substrates[144–146,150]

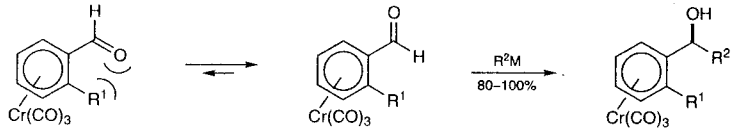


11 56 57 70% ee 58 99% ee

Diastereoselectivity of nucleophilic addition to *ortho*-substituted aryl aryl ketones or to *ortho*-substituted (aryl aldehyde)tricarbonylchromium complexes depends on the nature of the *ortho* substituent, the nucleophile and, if present, the Lewis acid. Addition to the carbonyl group in *ortho*-substituted (aryl aldehyde)tricarbonylchromium complexes involves an *exo* approach of the nucleophile, with the aldehyde adopting an *anti* conforma-

tion relative to the *ortho* substituent. The *syn* conformation is disfavored because of $A_{1,3}$ strain. This also holds for benzaldimine complexes. The example shown in Scheme 14 includes additions of Grignard reagents,[151,161,205] organolithium reagents,[152–154] and an organozinc reagent.[155]

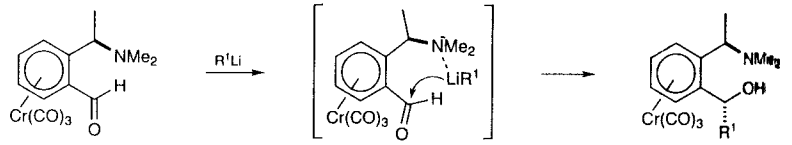
Scheme 14 Diastereoselective Nucleophilic Addition to *ortho*-Substituted (Aryl aldehyde)tricarbonylchromium Complexes[151–155,161,205]



R^1	R^2	MR^2	de (%)
Me	Et	EtMgBr	100
Me	Me	MeLi	100
Me	C≡CTMS	LiC≡CTMS	100
OMe	Ph	PhMgBr	100
OMe	CH_2CN	$NCCH_2ZnBr$	80
OMe	C_2F_5	C_2F_5Li	92

Complex **60**, obtained via diastereoselective lithiation of the complexed phenylethylamine **107** (see Scheme 39), reacts with methyllithium via a chelate intermediate with moderate diastereoselectivity to give product **61** (Scheme 15). The bulkier *tert*-butyllithium gives better diastereoselectivity but the product is obtained in low yield.[156]

Scheme 15 Nucleophilic Addition[156]



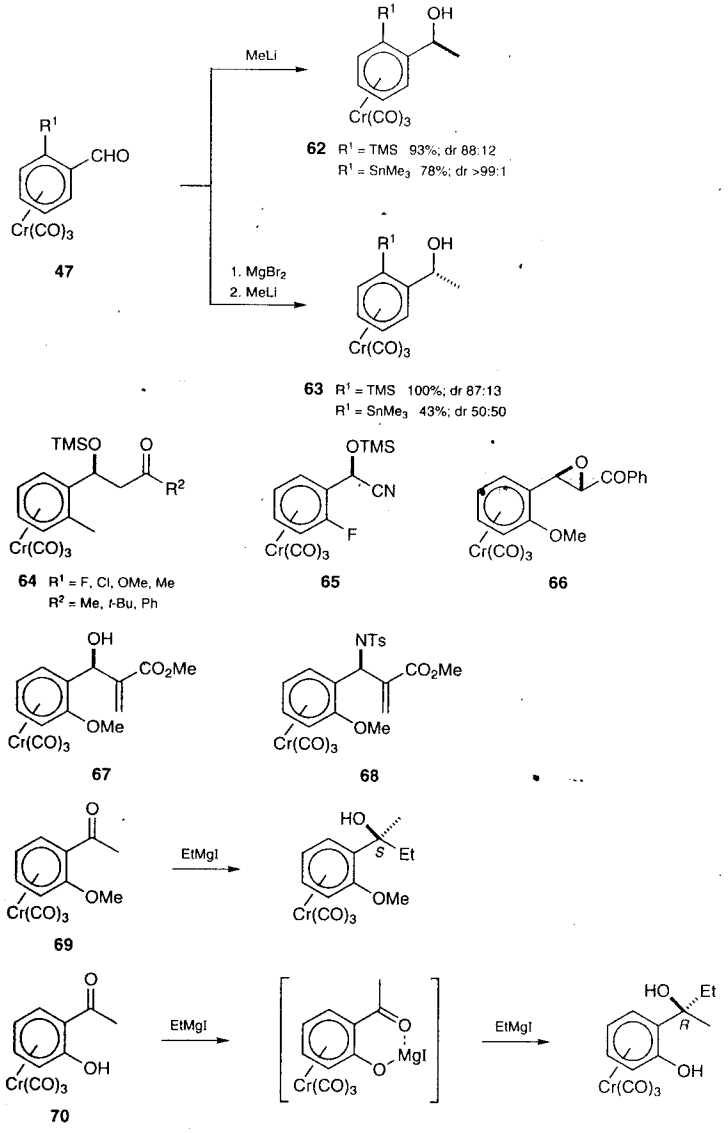
60

61 R^1 = Me 62%; 62% de
R^1 = *t*-Bu 32%; 98% de

Complexes **47** (R^1 = TMS, $SnMe_3$) react with nucleophiles via the *syn*-conformer either because the approach of the nucleophile in the *anti*-conformer is hindered by the large substituent and/or because the *syn* conformation is preferred in the ground state (e.g., **47** → **62**),[52,157,369] see Scheme 16. The latter has been demonstrated and is believed to arise from a Lewis acid/base interaction between the aldehyde function and the *ortho* substituent.[161,162] Addition of a Lewis acid [magnesium bromide, titanium(IV) chloride, boron trifluoride] activates the carbonyl group and also increases its bulk, thereby enforcing the *anti* conformation and reversing the diastereoselectivity (e.g., **47** → **63**).[52,159,369] Other examples of highly diastereoselective additions to the *anti*-conformer of *ortho*-substituted (aryl aldehyde)tricarbonylchromium(0) complexes are the triflate catalyzed addition of enol silanes to give **64**,[370] the cyanohydrin formation to give **65**, the Darzens reaction between phenacyl chloride and the anisaldehyde complex (+)-**47** (R^1 = OMe) to give the *trans*-epoxide **66**,[158] and the Baylis–Hillman reaction to give **67**[159] and **68**.[160] Reactions of aryl methyl ketones **69** also give the diastereomer resulting from addition to the *anti* conformation of the oxo group relative to the *ortho* substituent.[161] In contrast, addition to the

corresponding phenols **70** gives products arising from addition to the *syn* conformation, via a chelation-controlled pathway.[161,162]

Scheme 16 Diastereoselective Nucleophilic Addition to *ortho*-Substituted Benzaldehyde and Arylketone Tricarbonylchromium Complexes[52,157–162]



(-)-[(*S,S*)-Tricarbonyl[η⁶-2-methoxy(α-phenyl)benzyl alcohol]chromium(0) (59, R^1 = OMe; R^2 = Ph); **Typical Procedure:**[205]

A soln of (+)-[$Cr(CO)_3$(η⁶-*o*-anisaldehyde)] (**47**, R^1 = OMe; 470 mg, 1.73 mmol) in THF (4 mL) was cooled to −78 °C. Then 0.78 M PhMgBr in Et_2O (6.65 mL, 5.19 mmol) was added dropwise and the mixture was stirred for 1 h at −78 °C. An excess of MeOH was added slowly to quench the anion, the temperature was raised to rt, and the solvents were evaporated.

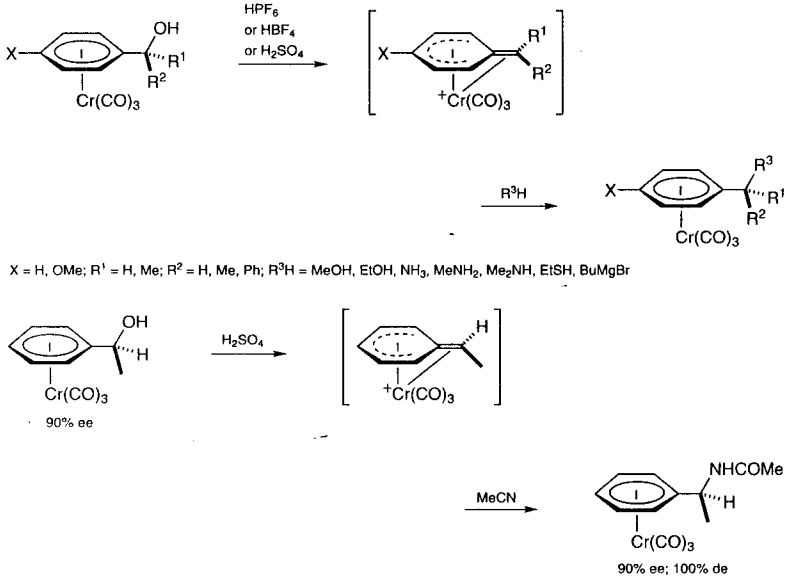
The residue was purified by column chromatography (alumina, Et_2O), giving the product as a yellow solid; yield: 605 mg (100%); mp 113–114°C; $[\alpha]_D$ –178 (*c* 1.46, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$: 1970, 1888, 1606 cm^{-1}.

2.4.6.2 Variation 2: Via Benzylic Cations

Benzylic carbocations complexed to tricarbonylchromium are stabilized by delocalization of the positive charge onto the chromium. Benzylic leaving groups that can adopt a conformation antiperiplanar to the arene—chromium bond undergo facile cleavage. Rotation about the C_{Ar}—C_α bond is restricted in the cation. Nucleophilic substitution therefore occurs with retention of configuration.[114] Analysis using density functional theory supports the stabilization and the rotational barrier in the cationic intermediates.[137,163]

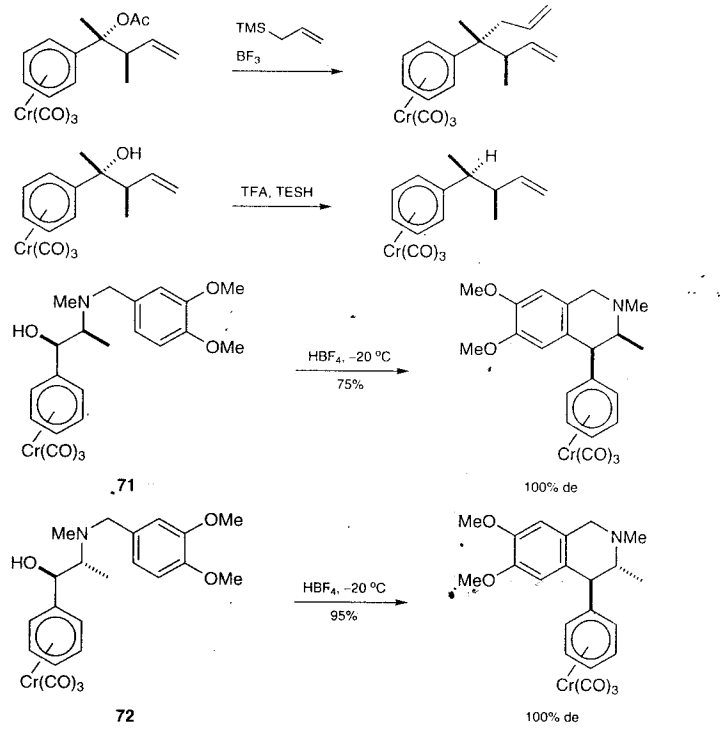
Treatment of (benzyl alcohol)tricarbonylchromium(0) complexes with strong acids, or of benzyl acetate derivatives with Lewis acids [such as zinc(II) chloride, boron trifluoride, or trimethylaluminum], generates the corresponding stabilized carbocations, which can be trapped by a range of nucleophiles including alcohols, amines, thiols, electron-rich arenes, nitriles (Ritter reaction), allylsilanes, and Grignard reagents (Scheme 17).[146,164–166] Overall retention of configuration results, except in cases where nucleophilic trapping is reversible or slower than rotation around the C_{Ar}—$C(R^1R^2)^+$ bond.

Scheme 17 Reactions of Benzylic Carbocations[146,164–166]



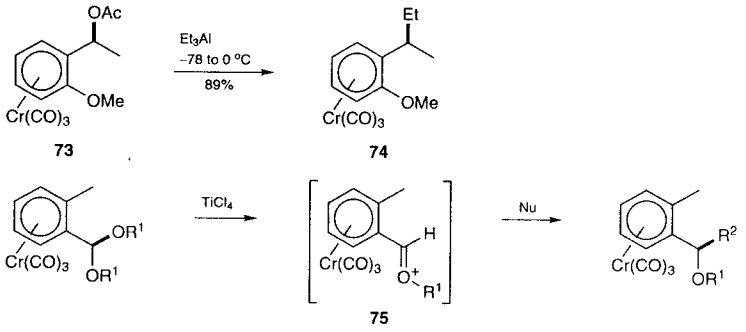
ortho Substituents and additional stereogenic centers do not influence the stereochemical outcome. Examples include both inter-[167] and intramolecular[168] nucleophilic trapping (Scheme 18). Ephedrine and pseudoephedrine derivatives **71** and **72** cyclize to stereospecifically generate *cis*- and *trans*-tetrahydroquinoline products, respectively.

Scheme 18 Further Reactions of Benzylic Carbocations[167,168]

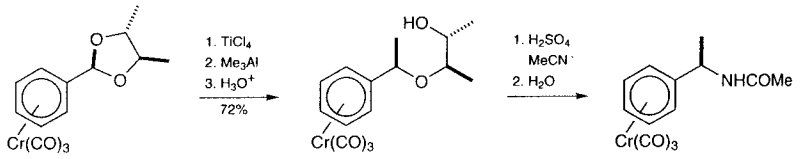


In cases where the leaving group cannot adopt an *anti* geometry, as in *endo*-tetral-1-ol[144,169] or *endo*-indan-1-ol[170,171] complexes, ionization can still occur, but is much slower than with the *exo* analogues. Trapping of the carbocation by nucleophiles occurs from the *exo* face, leading to an overall inversion of configuration. In the case of tertiary alcohols, strong nucleophiles (e.g., triethylsilane, allylsilane) are required to avoid elimination reactions.[108] In the acyclic *ortho*-substituted series, e.g. **73** (Scheme 19), *exo* elimination is preferred even if it requires the formation of a more strained carbocation, though epimerization occurs if nucleophilic trapping is not fast enough.[74]

Scheme 19 Carbocations via Ionization of Acetals[172,173]



R^1	Nu	R^2	Yield (%)	de (%)	Ref
Me	Me_3Al	Me	80	99	[172]
Me	EtOH	OEt	85	96	[172]
Et	MeOH	OMe	76	94	[172]

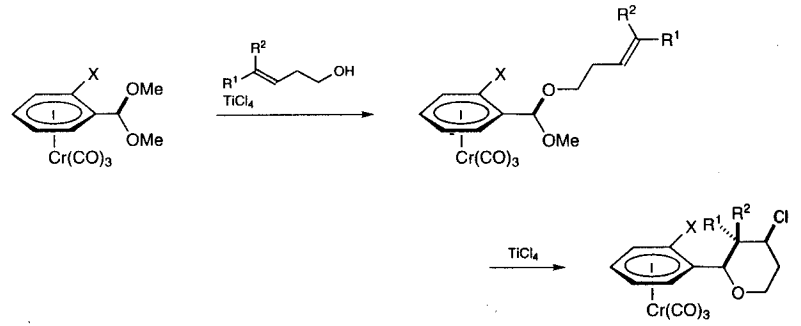


(*R*,*R*)-**76** (*R*)-**77** >98% de

Acetal cleavage with Lewis acids affords oxonium ions such as **75** (Scheme 19). These reactions proceed through the more stable *anti* conformation, even if the *syn* conformation is generated initially in these intermediates (rotation about the C_{Ar}—C_{α} bond is facile). With different alkoxy groups, loss of the smaller group (better ligand for the Lewis acid) is preferred.[172] Sequential diastereoselective dioxolane ring opening–alkylation and ether hydrolysis–Ritter reaction in the chiral benzaldehyde acetal complex **76** provides a route to the (*R*)-*N*-acetyl-1-phenethylamine complex **77**.[173]

This methodology has found application in the highly stereospecific synthesis of 2-aryltetrahydropyran derivatives by repeated acetal ionization (Scheme 20).[174]

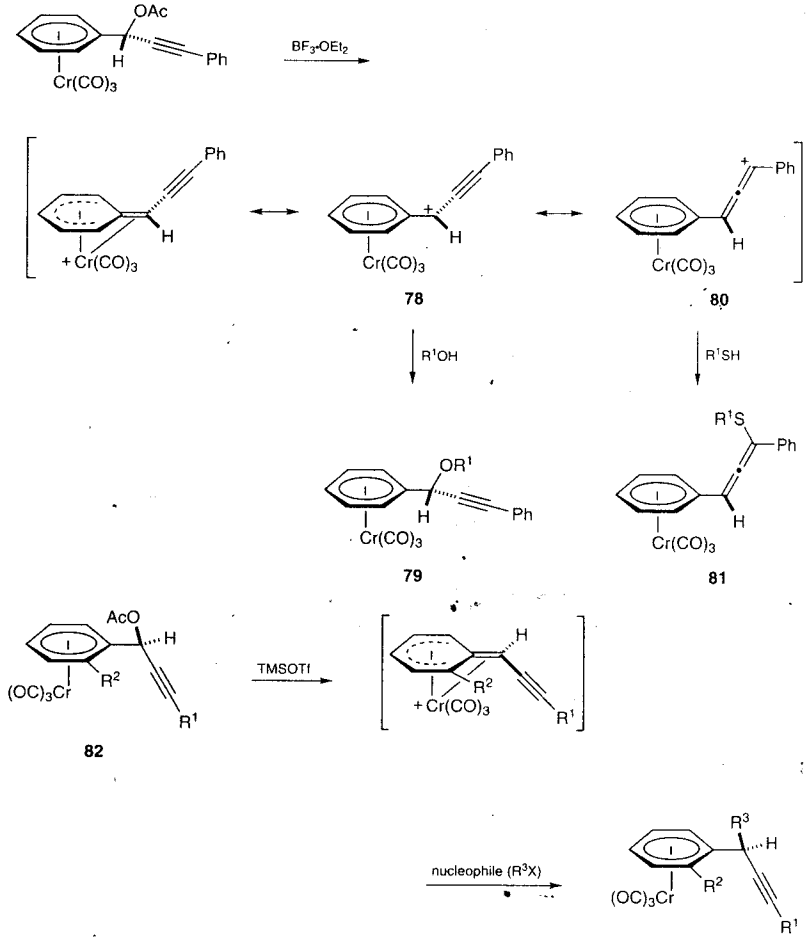
Scheme 20 Synthesis of Tetrahydropyran Derivatives[174]



X = Me, OMe; R^1 = R^2 = H, Me

The stabilized carbocation methodology has been applied to complexes bearing a propargylic substituent (Scheme 21). In this case, cleavage of benzylic acetate generates a doubly stabilized species, which can be described by two resonance structures **79** and **81**. Alcohols add to the benzylic position to yield the alkynyl product **78**, whereas thiols give only allenes **80** exclusively.[175] Surprisingly, if an *ortho* substituent is present, as in **82**, the sequence always gives only substitution at the benzylic position, with a global retention of configuration.[176]

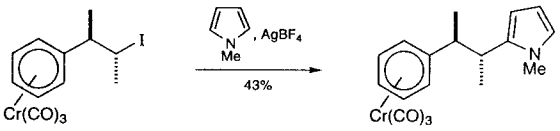
Scheme 21 Reactions of Complexes Bearing a Propargylic Substituent[175,176]



R^1 = Me, Ph; R^2 = Me, OMe; R^3 = NR^4_2, SR^5

Neighboring group participation by chromium is invoked to rationalize the high degree of **retention** shown in the example **83** → **84** in Scheme 22.[372] In a mesyloxy-substitution by **sodium** acetate at the γ-position the amount of retention product falls off sharply to 20%.

Scheme 22 Stereochemical Retention as Invoked by Chromium Neighboring Group Participation[372]



83 **84** 86% retention

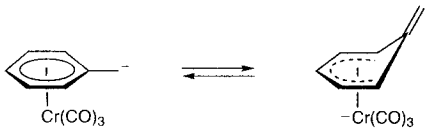
(*S*,*S*)-(1-*sec*-Butyl-2-methoxyphenyl)tricarbonylchromium(0) (74):[74]
To a soln of (*S*,*S*)-tricarbonyl[η⁶-2-methoxy(α-methyl)benzyl acetate]chromium(0) (**73**; **100 mg**, 0.3 mmol) in dry CH_2Cl_2 (6 mL) was added 1.0 M Et_3Al in hexane (1.2 mL, **1.2 mmol**) at −78 °C under argon. The mixture was warmed to 0 °C for 3 h, quenched with

cold dil HCl, and extracted with CH_2Cl_2. The extract was washed with sat. aq $NaHCO_3$ and brine, and dried ($MgSO_4$). Evaporation of the solvents and purification by column chromatography on silica gel gave the product; yield: 81 mg (89%); mp 84 °C; IR ($CHCl_3$) $\tilde{\nu}_{CO}$: 1960, 1870 cm^{-1}.

2.4.6.3 Variation 3: Via Benzylic Anions

The "$Cr(CO)_3$" moiety stabilizes benzylic carbanions by delocalization of the negative charge onto the "$Cr(CO)_3$" fragment. Substantial exocyclic C=C bond character exists, with the benzyl ligand being η^5 bound to the "$Cr(CO)_3$" fragment (Scheme 23).[137,163]

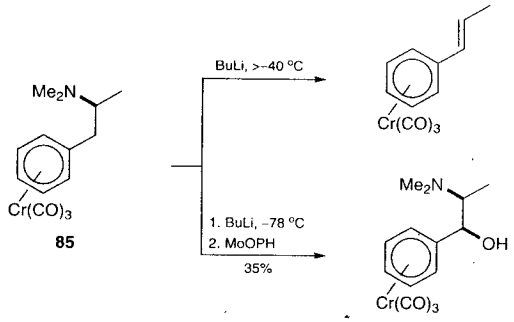
Scheme 23 Stabilization of a Benzylic Carbanion by the "$Cr(CO)_3$" Fragment[137,163]



The complexation renders the benzylic protons more acidic than in the free arenes. Deprotonation can be effected with bases such as alkoxides, potassium hydride, or lithium diisopropylamide. Competition with aryl—hydrogen deprotonation and aryl addition can occur with alkyllithium reagents and lithium diisopropylamide, especially when substituents that promote *ortho* deprotonation are present on the arene. In most cases, however, the thermodynamic anion is formed at the benzylic position, and can be trapped with a variety of electrophiles. Normal substituent effects apply in the benzylic deprotonation. Thus, *meta* substituents have essentially no effect, *ortho* and *para* acceptor groups (CO_2R, TMS) increase the benzylic acidity, while *ortho* and *para* donors (OMe, Cl, NMe_2) decrease it.

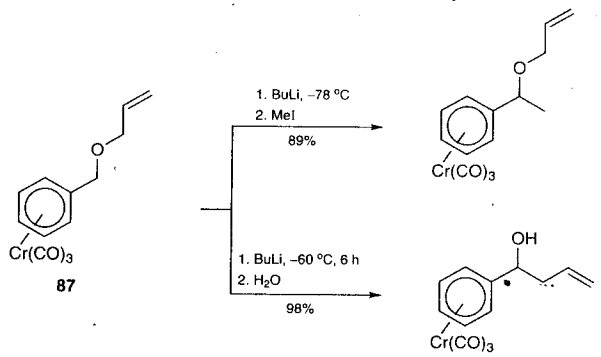
The increased stability of benzylic carbanions is not sufficient to prevent elimination processes, which generate the corresponding styrene complexes if a suitable β-leaving group is present (Scheme 24). β-Amino groups are eliminated at room temperature, but below –40 °C the carbanion is stable and can be quenched by a range of electrophiles.[177] In this case, both the deprotonation and the electrophilic quench have been shown to proceed stereospecifically, with chelation-controlled *exo* removal of the *pro-R* benzylic hydrogen antiperiplanar to the aryl—chromium bond. This generates a configurationally stable benzylic carbanion, which is quenched *exo* to the chromium to give overall retention of configuration. Reactions of this type are well studied and find numerous synthetic applications, both in the cyclic and in the acyclic series.[101,178] This process allowed the stereoselective conversion of the (*S*)-(+)-*N*,*N*-dimethylamphetamine complex **85** into the (1*S*,2*S*)-(+)-*N*-methylpseudoephedrine derivative **86** (Scheme 24).

Scheme 24 Reactions of Benzylic Carbanions[101,177,178]



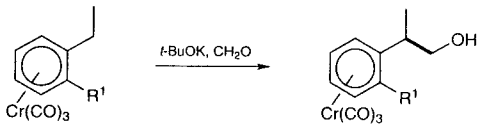
exo Deprotonation is faster than *endo* deprotonation. However, *endo* protons can be removed when no *exo* protons of comparable acidity are present. Stabilization of the benzylic carbanion suppresses the Wittig rearrangement in (alkyl benzyl ether)tricarbonylchromium(0) complexes. This is even true in the case of the (allyl benzyl ether)tricarbonylchromium(0) complex **87**, provided that the temperature is kept at –78 °C and the anion is quenched rapidly (Scheme 25).[146]

Scheme 25 Electrophilic Quench versus Wittig Rearrangement[146]

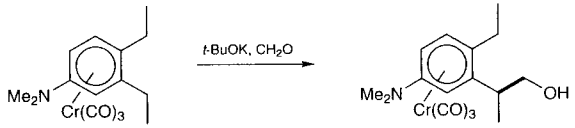


Benzylic deprotonation in planar chiral complexes can be highly diastereoselective, as shown in the transformations **88** → **89** and **90** → **91** (Scheme 26).[179,180] In the later case, the inductive effect of the dimethylamino group favors deprotonation of the *meta* over the *para* ethyl group.

Scheme 26 Diastereoselectivity in Benzylic Carbanions Reactions[179,180]



R^1	Yield (%)	de (%)	Ref
OMe	66	82	[180]
OiPr	45	100	[180]
NMe_2	85	92	[180]
NEt_2	88	100	[180]



90 91

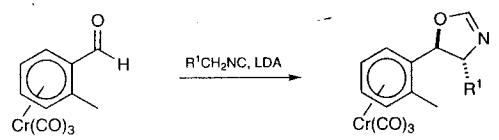
Tricarbonyl{2-[η⁶-2-(diethylamino)phenyl]propan-1-ol}chromium(0) (89, $R^1 = NEt_2$); General Procedure:[180]

Tricarbonyl(η⁶-2-ethyl-*N*,*N*-diethylaniline)chromium (**88**, $R^1 = NEt_2$; 0.6 mmol), *t*-BuOK (0.8 mmol), HCHO (0.8 mmol), and DMSO (2 mL) were mixed together at rt. After 0.5 h, the mixture was hydrolyzed with aqueous acid and extracted. Purification by column chromatography on silica gel afforded the product; yield: 88% (100% de); mp 78 °C; IR (CCl_4) $\tilde{\nu}_{CO}$: 1965, 1890 cm^{-1}.

2.4.6.4 Variation 4: Via Cycloaddition Reactions

The conformational preference of alkene, carbonyl, imine, and nitrone substituents in *ortho*-substituted arene complexes can be exploited in a variety of diastereoselective cycloaddition reactions. One enantioface of these functions being blocked by the "$Cr(CO)_3$" group, cycloaddition reactions are generally highly diastereoselective. Aryl-substituted β-lactams are formed highly diastereoselectively from reactions of "$Cr(CO)_3$" complexes of *ortho*-substituted arylaldehyde-derived imines with an in situ generated ketene.[181,182] The diastereoselective formation of oxazolines **92** involves a nucleophile addition–cyclization sequence (Scheme 27).[183]

Scheme 27 Formation of Oxazolines[183]

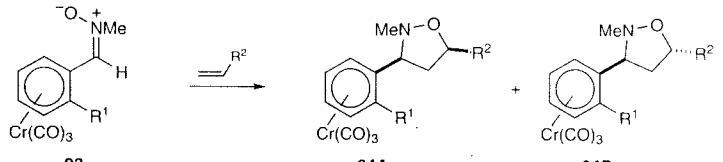


92

Arylaldehyde-derived nitrones undergo dipolar [3 + 2] cycloadditions with alkenes to give *cis*-2,5-disubstituted isoxazolidines.[184,185] In the example in Scheme 28, the relative stereochemistry of the newly formed benzylic stereogenic center is completely controlled by the planar chirality of the complex. This methodology has been extended to intramolecular reactions.[186] Arene complexes can also be the dipolarophile component in these reactions: nonracemic *ortho*-substituted tricarbonyl(styrene)chromium(0) complexes react with nitrile oxides to give 3,5-disubstituted 4,5-dihydroisoxazoles with good to excellent diastereoselectivity;[187] and enantiomerically pure benzaldehyde imine complexes

react with methyl acrylates to give chiral, nonracemic, trisubstituted "$Cr(CO)_3$"-complexed arylpyrrolidines. Regioselectivity in these reactions can be controlled by the Lewis acid used (Scheme 29).[188]

Scheme 28 [3 + 2] Cycloadditions with Complexed Nitrones[184,185]

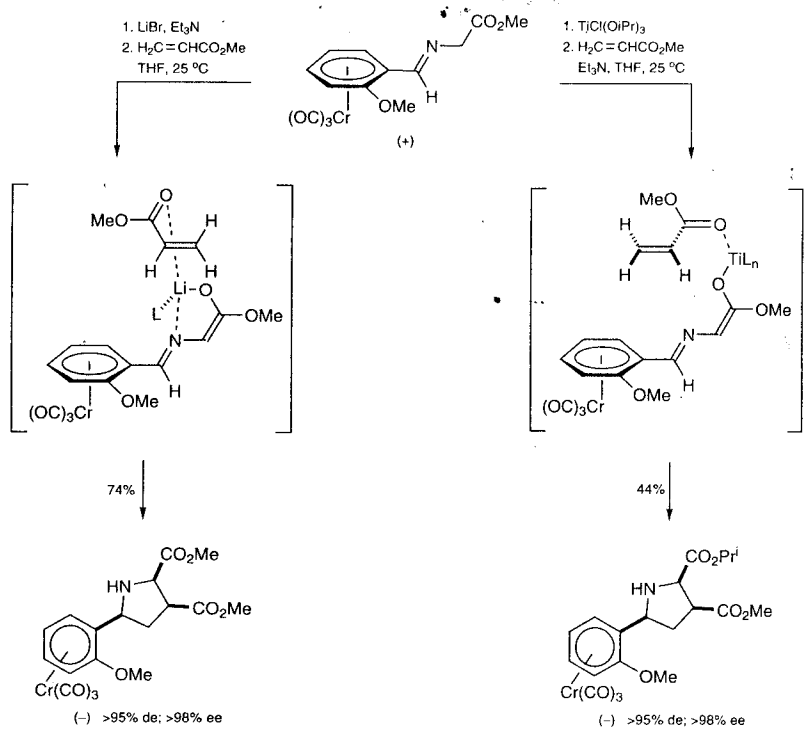


93 94A major 94B minor

R^1	R^2	Yield (%)	dr[a]	R^1	R^2	Yield (%)	dr[a]
H	Ph	69	>98:2	TMS	Ph	80	>98:2
H	OEt	70	>98:2	TMS	OEt	63	>98:2
H	OAc	51	74:26	TMS	OAc	85	>98:2
H	TMS	15	86:14	TMS	TMS	42	80:20

[a] dr refers to the stereochemistry of isoxazolidine ring.

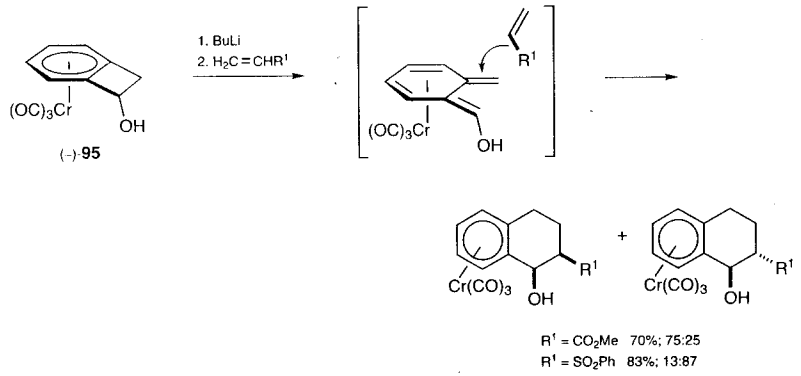
Scheme 29 [3 + 2] Cycloadditions with Complexed Benzaldehyde Imines[187,188]



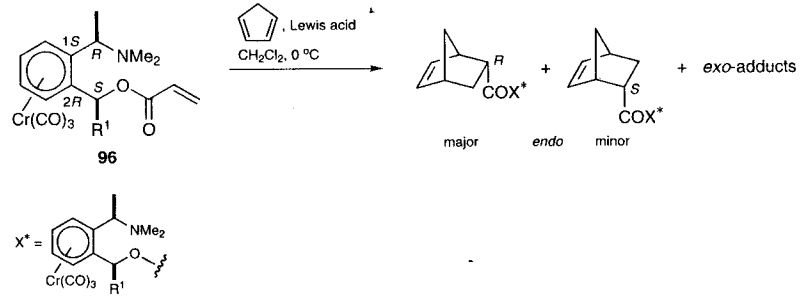
Planar chirality has been successfully used in Diels–Alder reactions. A chiral, nonracemic *ortho*-quinodimethane complex intermediate can be generated by anion-accelerated electrocyclic ring-opening from the 1-hydroxycyclobutabenzene complex **95** (Scheme 30). When carried out in the presence of an activated alkene ($R^1 = CO_2Me$, SO_2Ph), *exo*-tetralol complexes are formed exclusively.[189,190,221] Scheme 31 shows an example of a diastereo-

elective Diels–Alder reaction where a chiral tricarbonylchromium complex is the dienophile component.[191] In this case, the chromium complex **96** is used as a chiral auxiliary.

Scheme 30 Diels–Alder Reactions[189,190,221]



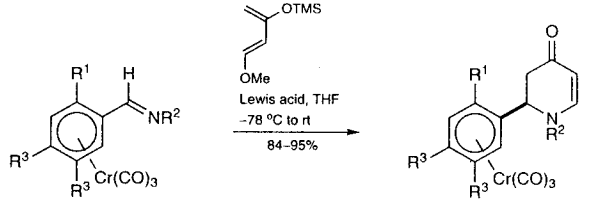
Scheme 31 Further Diels–Alder Reactions[191]



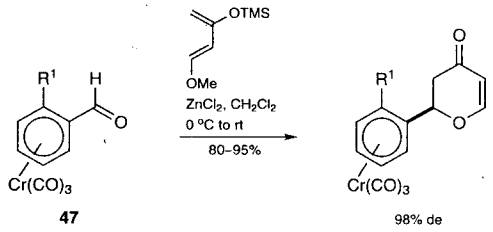
R^1	Lewis Acid	Yield (%)	Ratio (*endo*/*exo*)	de (%) of *endo* Adducts
Ph	$Sn(OTf)_2$	61	88:12	88
α-naphthyl	$ZnCl_2$	80	>99:1	>99
β-naphthyl	$ZnCl_2$	75	96:4	76
2,4,6-$Me_3C_6H_2$	ZnI_2	60	>99:1	>99
Et	$MgBr_2$	66	>99:1	3

Aza Diels–Alder cycloadditions with planar chiral arene(tricarbonyl)chromium(0) complexes include reactions with the complex being the diene[192] or the dienophile component (Scheme 32).[193] With the latter, diastereoselectivity is influenced also by the Lewis acid used, and tin(IV) chloride and diethylaluminum chloride have proven best. Analogous cycloadditions are feasible with the *ortho*-substituted benzaldehyde complexes **47**.[194]

Scheme 32 Hetero Diels–Alder Reactions[193]



R^1	R^2	R^3	Lewis Acid	Yield (%)	dr
Cl	–	H	$ZnCl_2$	95	>98:2
Me	–	H	$ZnCl_2$	91	>98:2
OMe	–	H	$ZnCl_2$	80	>98:2
Cl	Bn	H	$ZnCl_2$	88	89:11
Cl	Bn	H	$SnCl_4$	98	>98:2
OMe	Bn	H	$ZnCl_2$	82	83:17
OMe	Bn	H	$SnCl_4$	82	86:14
Cl	$(CH_2)_3OH$	OMe	$SnCl_4$	70	>98:2
TMS	$(CH_2)_3OH$	OMe	$SnCl_4$	48	>98:2



(3*R*,5*S*,1′*R*)-Tricarbonyl{2-methyl-5-phenyl-3-[η⁶-2-(trimethylsilyl)phenyl]isoxazolidine}-chromium(0) (94A, R^1 = TMS; R^2 = Ph):[185]

Nitrone complex **93** (76 mg, 0.22 mmol) and styrene (3 mL, 26 mmol) were heated in a sealed tube at 90 °C for 6 h. Excess styrene was removed by evaporation and the crude cycloadduct was purified by column chromatography to provide the product as a yellow oil; yield: 78 mg (79%); IR ($CHCl_3$) $\tilde{\nu}_{CO}$: 1970, 1900 cm^{-1}.

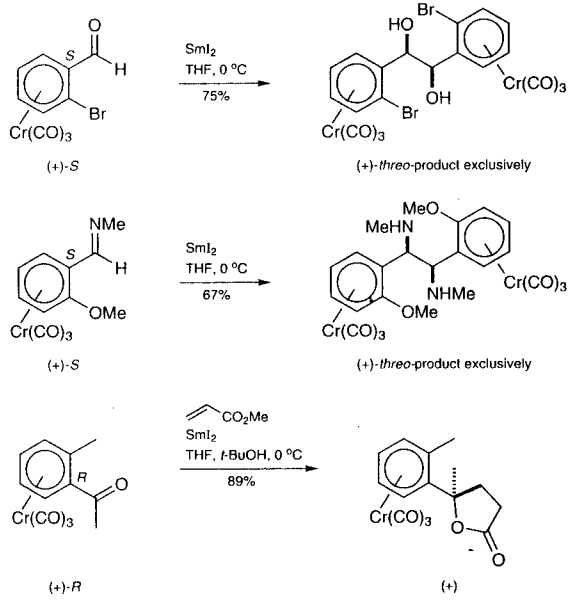
(1*S*,2′*S*)-(+)-2-{[4,5-Dimethoxy-2-(trimethylsilyl)phenyl]tricarbonylchromium}-1-(3-hydroxypropyl)-2,3-dihydropyridin-4(1*H*)-one [98, R^1 = TMS; R^2 = $(CH_2)_3OH$); R^3 = OMe]; Typical Procedure:[195]

$SnCl_4$ (1.02 mL, 8.80 mmol, 1.6 equiv) was added dropwise to a cooled (–78 °C) soln of the imine complex **97** (2.38 g, 5.5 mmol) in THF (15 mL) and the mixture was stirred at –78 °C for 15 min. Danishefsky's diene (2.09 mL, 11 mmol, 2 equiv) was added and stirring continued (–78 to 0 °C, 18 h). Workup and column chromatography (silica gel, EtOAc) gave the product as an orange solid and a single diastereomer; yield: 1.35 g (48%); $[\alpha]_D$ +152 (*c* 0.53, $CHCl_3$); IR (CH_2Cl_2) $\tilde{\nu}_{max}$: 1955, 1877, 1643, 1593 cm^{-1}; ^1H NMR (benzene-d_6, δ): 0.21 (s, 9H), 0.7 (br t, 1H), 1.35 (m, 2H), 1.40 (m, 2H), 2.45 (d, 1H), 2.90 (m, 2H), 3.20 (s, 3H), 3.30 (m, 2H), 3.35 (s, 3H), 3.50 (m, 1H), 4.30 (d, 1H), 4.91 (s, 1H), 5.10 (d, 1H), 5.68 (s, 1H), 6.35 (d, 1H).

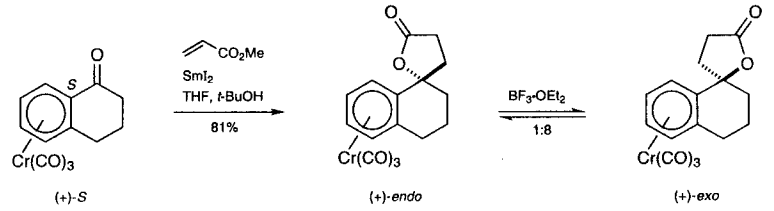
2.4.6.5 Variation 5: Via Radical Coupling Reactions

In addition to carbanions and carbocations, the "$Cr(CO)_3$" group also stabilizes benzylic radicals. This can lead to powerful synthetic methodology, particularly when used in combination with the strong asymmetric induction provided by planar chiral complexes. Samarium(II) iodide promoted radical reactions, including pinacol coupling of complexed aryl aldehydes[196] and aryl imines,[197] γ-butyrolactone formation from planar chiral aryl ketone complexes and methyl acrylate[198,371] are highlighted here (Scheme 33).

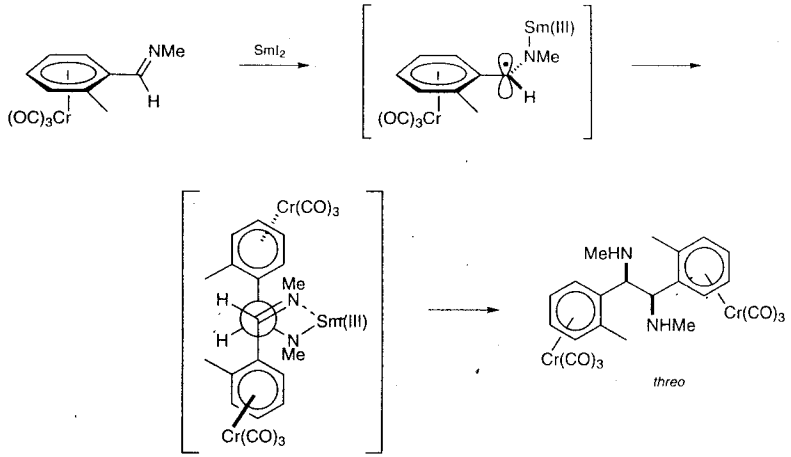
Scheme 33 Samarium(II) Iodide Promoted Radical Reactions[196–198,371]



The postulated mechanism of the aldehyde and imine coupling reactions shown in Scheme 34 is thought to involve a complexed benzylic radical. This intermediate, as supported by theoretical calculations,[137] has exocyclic C=C bond character with η^5-coordination of the ligand to the "$Cr(CO)_3$" fragment. The geometry adopted by the exocyclic C_{Ar}=C_α bond minimizes steric interactions between the arene *ortho* substituent and the Sm—O or Sm—N bond. Coupling via a chelation-controlled transition state then provides a rationale for the observed formation of *threo* products.



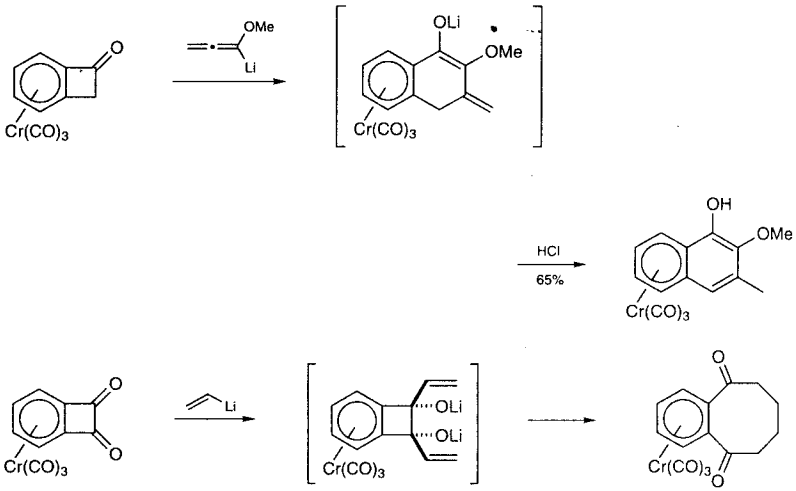
Scheme 34 Mechanism of Samarium(II) Iodide Promoted Radical Reactions[137]



2.4.6.6 Variation 6: Via Ring Expansion Rearrangements

Tricarbonylchromium(0) complexes of benzocyclobutenone and benzocyclobutenedione can undergo ring expansion reactions leading to substituted tetraol (see Section 2.4.6.5), naphthol, benzocycloheptenedione, and annulated indanone complexes.[189,373] The naphthol complexes shown are the products of an alkoxy anion accelerated vinylcyclobutene–cyclohexadiene rearrangement and benzocyclooctenedione complexes originate from a dianionic oxy-Copy rearrangement (Scheme 35).

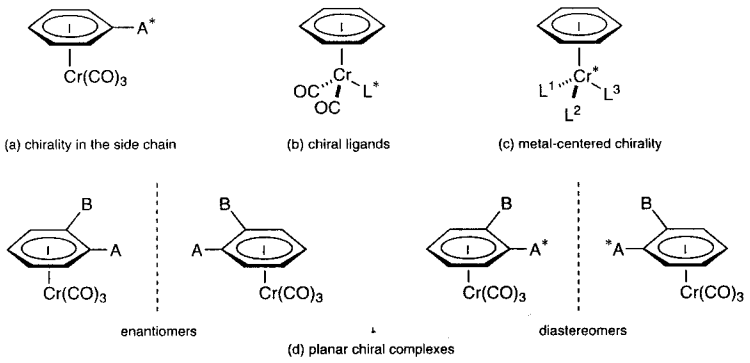
Scheme 35 Ring Expansion Rearrangements of Benzocyclobutenone and Benzocyclobutenedione Complexes[189,373]



2.4.7 Method 7: Synthesis of Optically Active Arene Complexes

The synthesis of optically active arene complexes has been developed only for chromium–arene complexes (for applications, see Section 2.4.10). Distinct categories in this class of compound are shown in Scheme 36. Chirality may be associated with (a) a stereogenic center in an aryl substituent, (b) a chiral ligand on the metal, (c) a stereogenic metal center, or (d) different *ortho* or *meta* arene substituents (planar chirality).

Scheme 36 Chiral Chromium–Arene Complexes



The literature contains complexes of all the above categories. Examples for (b) and (c) will be discussed in Section 2.4.8. In view of their importance, we will focus in this section on routes to nonracemic planar chiral arene(tricarbonyl)chromium complexes exclusively.[387] These compounds are increasingly finding applications as ligands in catalytic reactions[199] and as chiral building blocks in highly diastereoselective transformations (see Section 2.4.11). Routes to chiral nonracemic complexes can be divided into resolution of racemic complexes (see Section 2.4.7.1) and asymmetric syntheses (Sections 2.4.7.2 to 2.4.7.5). Of the latter, most approaches rely on transformations in which a chiral arene substituent controls the generation of planar chirality in the complex. These powerful, well-established diastereoselective transformations are complemented by a growing number of enantioselective methods, in which planar chirality in the product is generated by an external chiral agent.

2.4.7.1 Variation 1: Resolution of Racemates

Racemic complexes containing an amine or a carboxylic acid function have been resolved via formation of diastereomeric salts with chiral carboxylic acids such as (+)-camphorsulfonic acid (for *ortho*- and *meta*-toluidine complexes), or chiral amines such as brucine (for the *meta*-methoxybenzoic acid complex) followed by recrystallization.[200–203] For *ortho*-substituted benzaldehyde complexes, an early resolution procedure involved formation of diastereomeric semioxamazones, separation by column chromatography, and acid hydrolysis.[204] Another very efficient procedure uses L-valinol and column chromatography on alumina to separate the diastereomeric imines formed.[205] Enzymatic kinetic resolution procedures have been used mostly in enantioselective reductions of chiral aryl aldehydes.[206–208] Other examples include enzymatic ester hydrolysis,[209] and esterification reactions on benzylic alcohols[210–212] and oximes.[213] Many planar chiral complexes are readily resolved on commercial chiral HPLC columns.[214,215] Kinetic resolution of racemic

tricarbonyl(2-chloroanisole)chromium(0) via palladium-catalyzed asymmetric alkoxycarbonylation was achieved with 30% ee.[216]

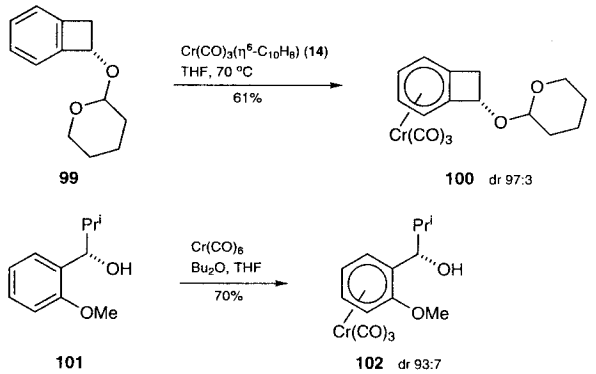
Resolution of (η⁶-*o*-Anisaldehyde)tricarbonylchromium(0) (47, R¹ = OMe); Typical Procedure:[205]

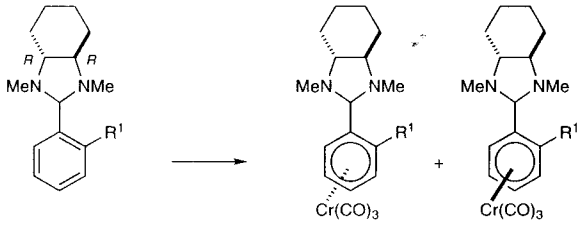
L-Valinol (379 mg, 3.68 mmol) was added to an Et_2O soln (10 mL) of complex **47** (1.00 g, 3.68 mmol) and the mixture stirred (4.5 h), the initial red soln turning orange. Column chromatography (alumina) of the crude soln without evaporation of the solvent gave two fractions. The first fraction (Et_2O) was evaporated to a red solid and the second fraction ($MeOH/CH_2Cl_2$ 1:10) to an orange oil. Both products were separately dissolved in THF (8 mL). Water (2 mL) was added followed by concd HCl (5 drops) and the darkened solns stirred until they turned crimson (30 min). Evaporation of the solvent followed by filtration of an Et_2O soln (10 mL) through a plug of alumina gave both products as red solids. The first fraction was (–)-**47** (R¹ = OMe); yield: 460 mg (46%); $[\alpha]_D$ –1015 (*c* 0.06, $CHCl_3$). The second fraction was (+)-**47** (R¹ = OMe); yield: 380 mg (38%); $[\alpha]_D$ +1016 (*c* 0.06, $CHCl_3$).

2.4.7.2 Variation 2: Diastereoselective Complexation

Diastereofacial differentiation in the complexation of a chiral arene can be a powerful method. Bulky alkyl groups can direct the "$Cr(CO)_3$" group onto the *anti* face.[217] Conversely, functional groups at a stereogenic center will direct the "$Cr(CO)_3$" group preferentially into the *syn* face of the aromatic ring. This is effective only if the functional group is able to precoordinate the incoming "$Cr(CO)_n$" fragment and if the stereogenic center orients the guiding group toward one of the diastereotopic arene faces. Based on early findings by Jackson and Mitchell,[53] the most common case is a benzylic alcohol or ether group that is conformationally restricted either by a ring structure (tetralol, indanol) or by an aryl *ortho* substituent.[73,74,143,218,219,221] Other examples involve chiral acetals,[222] chiral aminals,[223] or a remote hydroxyl group.[224] Representative examples (**99** → **100**[221] and **101** → **102**[74]) are shown in Scheme 37. Best results are often obtained using mild reaction conditions such as arene exchange with tricarbonyl(naphthalene)chromium(0), thus favoring the kinetic product. An almost complete inversion of diastereofacial selectivity on using either kinetic (arene exchange at room temperature in tetrahydrofuran) or thermodynamic conditions [hexacarbonylchromium(0), 140 °C] was reported for **103**.[223]

Scheme 37 Diastereoselective Complexation of Chiral Arenes[74,221,223]



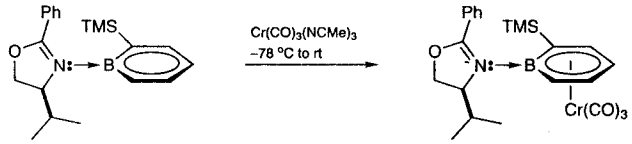


(*R,R*)-**103** (*2S*)-**104** (*2R*)-**104**

R^1	Reaction Conditions	Ratio [(2*S*)-**104**/(2*R*)-**104**]	Ref
Me	$Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ (**14**), THF, rt	97:3	[223]
OMe	$Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ (**14**), THF, rt	98:2	[223]
Me	$Cr(CO)_6$, Bu_2O, THF	12:88	[223]
OMe	$Cr(CO)_6$, Bu_2O, THF	9:91	[223]

Diastereoselective complexation has also been applied successfully to heterocyclic chemistry.[225,226] As shown in Scheme 38, the Lewis acid–base complex between an *ortho*-substituted borabenzene and an enantiomerically 'pure oxazoline was complexed to the "$Cr(CO)_3$" group using $[Cr(CO)_3(NCMe)_3]$, leading to the single diastereomer **105**. Since the chiral auxiliary is easily removed in this case, the methodology has the potential to lead to an enantioselective complexation with a catalytic use of the chiral auxiliary.[226]

Scheme 38 Diastereoselective Complexation of an Heteroarene via a Chiral Lewis Acid–Base Complex[225,226]



105

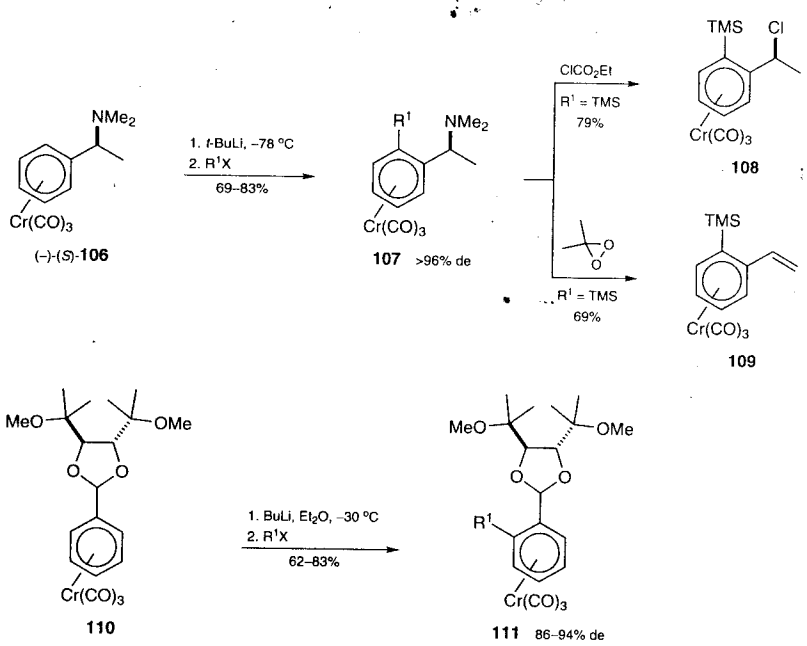
(2*S*)-1,3-Dimethyl-2-[tricarbonyl(η⁶-2-tolyl)chromium]octahydro-1*H*-benzimidazole (104, **R^1 = Me**):[223]

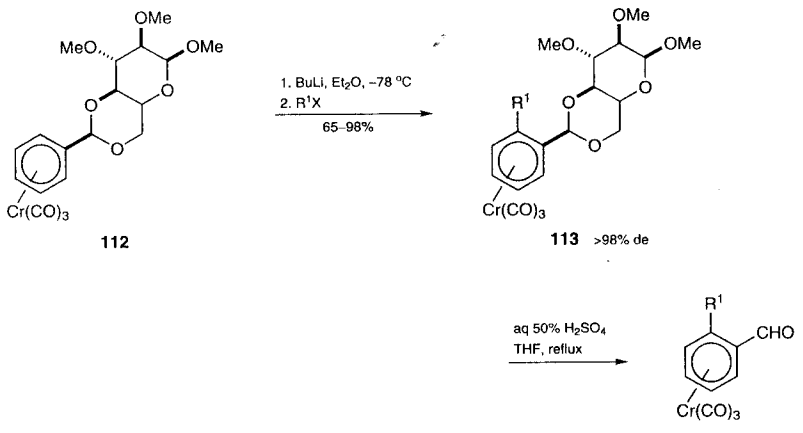
A mixture of the aminal (*R,R*)-**103** (120 mg, 0.49 mmol) and $[Cr(CO)_3(naphthalene)]$ (**14**; 129 mg, 0.49 mmol) in THF was stirred for 4 days at rt under an inert atmosphere. The solvents were removed in vacuo to give a yellow powder. As judged by ^1H NMR spectroscopy of the crude mixture, the two diastereomers 2*S* and 2*R* were formed in 97:3 ratio (R_f 0.55 and 0.45, respectively, in petroleum ether/Et_2O 85:15). Filtration of this mixture (silica gel, hexane/EtOAc 80:20 with 1% Et_3N) gave a yellow soln of the two diastereomers in the same ratio as above; yield: 149 mg (80%). Flash chromatography (silica gel, hexane/EtOAc 85:15) gave the major product (2*S*)-**104** as a yellow crystalline powder, mp 156–160 °C (dec); ^1H NMR ($CDCl_3$, δ): 1.17–2.04 (m, 9H), 2.30 (s, 3H), 2.38 (s, 3H), 2.80 (m, 1H), 3.52 (s, 1H), 4.88 (d, 1H), 5.07 (t, 1H), 5.51 (t, 1H), 5.86 (d, 1H).

2.4.7.3 Variation 3: Diastereo- and Enantioselective Lithiation–Electrophilic Addition Reactions

The deprotonation–electrophilic addition sequence has been detailed in Section 2.4.5.1. Scheme 39 shows a number of diastereoselective applications of the directed *ortho*-metalation methodology[227] to the synthesis of nonracemic planar chiral (arene)tricarbonylchromium(0) complexes. A Lewis basic function at a stereogenic center coordinates the lithium base and directs it to selectively remove one of the two diastereotopic hydrogens in the *ortho* position. The lithiated complex then reacts with an electrophile to give the chiral nonracemic complex. This approach is analogous to that used extensively in the synthesis of planar chiral ferrocenes[228] and was first applied to (*S*)-α-methylbenzylamine derivatives such as **106**.[156,164,229–231] The benzylic amine function in **107** can be converted into the chloride **108** with retention of configuration.[232] Alternatively, treatment with dimethyldioxirane affords the planar chiral styrene complex **109**.[233] For benzaldehyde complexes, the conversion into chiral nonracemic acetals[82,222,234,235] or aminals,[236,237] followed by lithiation–electrophilic addition, has been used extensively. With tartrate-derived acetals, e.g. **110**, regeneration of the aldehyde function without cleaving the aryl—chromium bond is problematic, but hydrolysis apparently poses no problem in the carbohydrate-derived acetal complex **111**.[235] Aminals are hydrolyzed under very mild conditions.[236]

Scheme 39 Diastereoselective Lithiation–Electrophilic Addition Reactions[156,164,229–233,235]



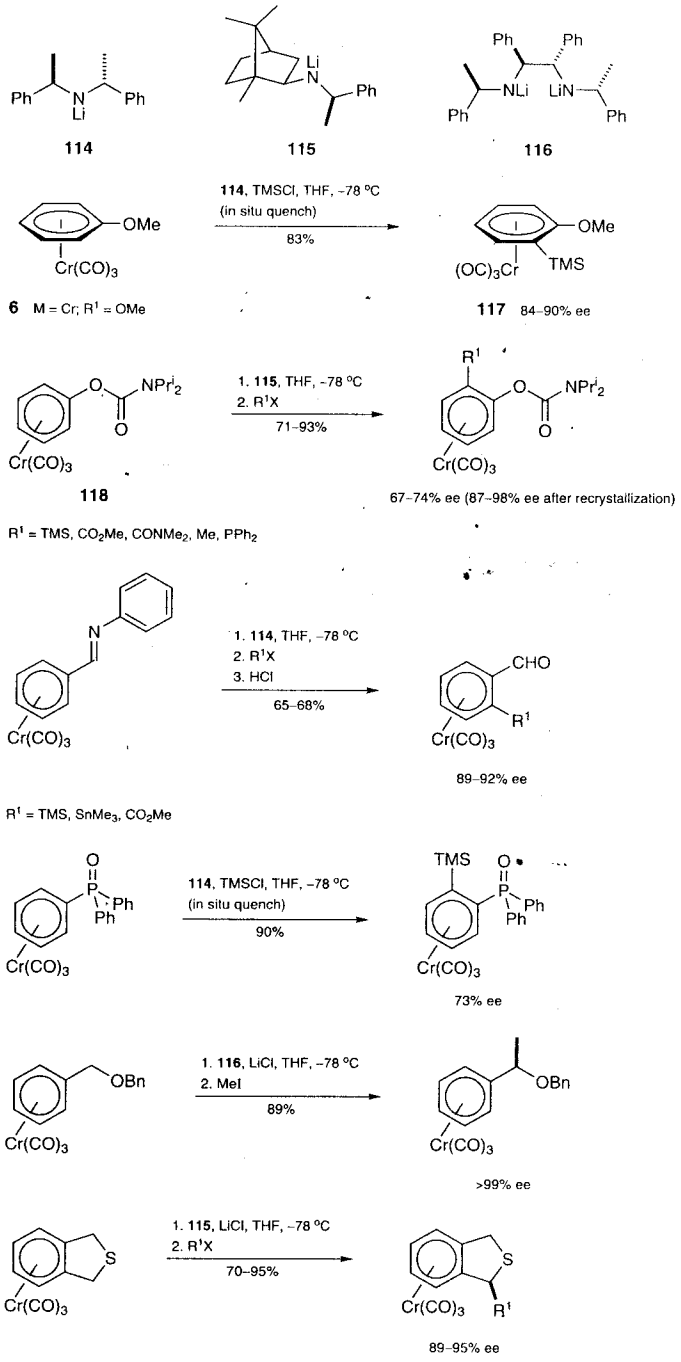


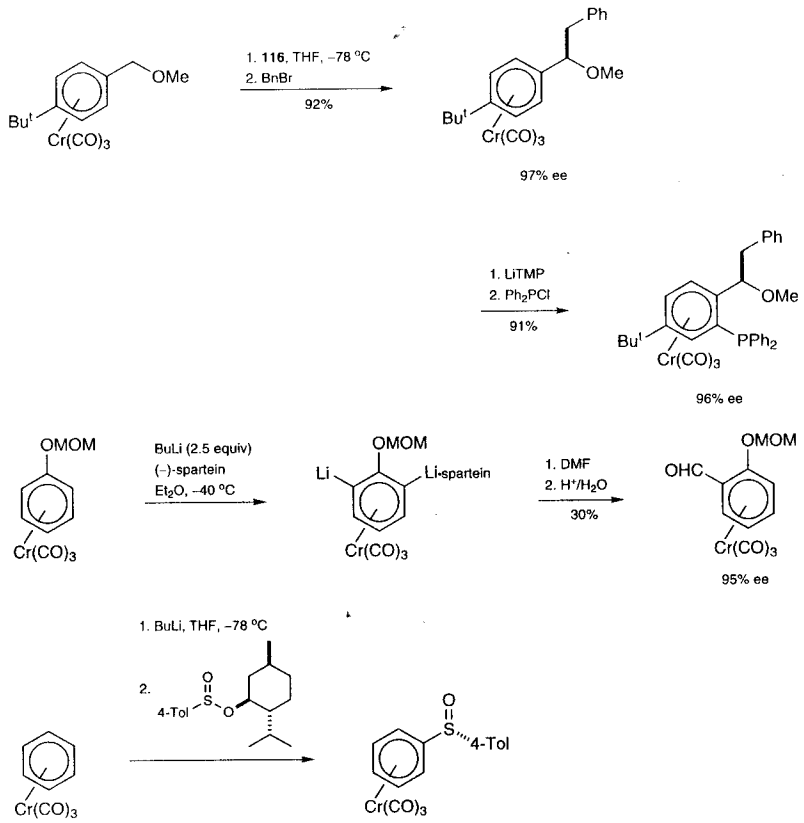
112

Complex	Electrophile (R^1X)	Product	R^1	Yield (%)	de (%)
106	MeSSMe	**107**	SMe	81	>96
106	Ph_2PCl	**107**	PPh_2	69	>96
106	TMSCl	**107**	TMS	70	>96
106	ICH_2CH_2I	**107**	I	83	>96
110	PhSSPh	**111**	SPh	74	92
110	Ph_2PCl	**111**	PPh_2	69	94
110	TMSCl	**111**	TMS	77	86
110	Bu_3SnCl	**111**	$SnBu_3$	73	91
110	$BrCH_2CH_2Br$	**111**	Br	68	88
110	MeI	**111**	Me	62	92
112	PhSSPh	**113**	SPh	80	>98
112	Ph_2PCl	**113**	PPh_2	74	>98
112	TMSCl	**113**	TMS	73	>98
112	Bu_3SnCl	**113**	$SnBu_3$	73	>98
112	MeI	**113**	Me	65	>98

Enantioselective synthesis of chiral (arene)tricarbonylchromium complexes via arene lithiation is shown in Scheme 40. *ortho*-Lithiation of prochiral complexes is carried out most frequently with enantiopure lithium amides, e.g. **114–116**,[238] although analogous reactions, though often with lower product enantiomeric excesses, have also been reported with alkyllithium bases in the presence of chiral amine ligands (e. g., spartein).[239,374,377] The C_2 symmetric base **114** deprotonates [Cr(anisole)$(CO)_3$] in the presence of chlorotrimethylsilane to give complex **117** with 84% ee (Scheme 40),[240] a value that was subsequently raised to 90% ee.[241,242] In situ quench conditions are required with this complex as the lithiated complex is not configurationally stable. The same base gives only 39% ee with the carbamate complex **118** and the major product is of opposite chirality. In this case, use of base **115** is more successful and the configurationally stable lithiated complex can be trapped with a variety of electrophiles to afford *ortho*-substituted complexes with ca. 70% ee.[243] Crystallization of the enantiomerically enriched complexes significantly increases the enantiomeric excess. Further examples and extensions to enantioselective benzylic deprotonations are shown in Scheme 40.[118,244,245]

Scheme 40 Enantioselective Synthesis of Chiral (Arene)tricarbonylchromium Complexes via Arene Lithiation[145,375–378]





Tricarbonyl[η⁶-2-(*S*)-(trimethylsilyl)benzaldehyde]chromium(0) (47, R¹ = TMS):[235]

Methyl 2,3-Di-*O*-methyl-4,6-*O*-(tricarbonyl[η⁶-2-(trimethylsilyl)benzylidene]chromium)-α-D-glucopyranoside (113, R¹ = TMS):

Complex **112** (0.20 g, 0.45 mmol) was dissolved in Et_2O (20 mL) and the soln cooled to −78 °C. BuLi (0.54 mmol) was added dropwise over 30 s. The resulting soln was stirred for 1 h at −78 °C and treated with TMSCl (5 equiv). After stirring for an additional 1 h at −78 °C, the soln was allowed to warm to rt. After quenching with aq 1 M NaOH, the organic layer was separated and purified by chromatography (hexane/Et_2O 2:1) to give **113** (R¹ = TMS); yield: 0.17 g (73%, >98% de); $[\alpha]_D$ +73 (*c* 0.20, $CHCl_3$); IR (neat) $\tilde{\nu}_{CO}$: 1955, 1854 cm^{-1}.

Tricarbonyl[η⁶-2-(*S*)-(trimethylsilyl)benzaldehyde]chromium(0) (47, R¹ = TMS):

Complex **113** (R¹ = TMS; 0.70 g, 0.13 mmol) was dissolved in THF (5 mL). Aq H_2SO_4 (50%, 0.5 mL) was added, and the resulting mixture was heated at reflux for 2 h. After cooling and neutralization with aq $NaHCO_3$, the organic layer was separated and purified by chromatography (hexane/Et_2O 20:1) to give **47** (R¹ = TMS); yield: 0.35 g (quant); $[\alpha]_D$ −145 (*c* 0.17, $CHCl_3$); IR (neat) $\tilde{\nu}_{CO}$: 1968, 1894 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.43 (s, 9H), 5.43 (d, 1H), 5.52 (t, 1H), 5.58 (t, 1H), 5.80 (d, 1H), 9.74 (s, 1H).

(2*R*)-(+)-Tricarbonyl[η⁶-2-(trimethylsilyl)anisole]chromium(0) (117); Typical Procedure:[244]

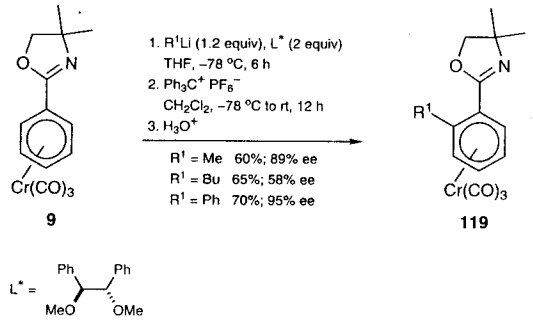
A soln of the enantiopure lithium amide **114** was prepared from the corresponding amine (248 mg, 1.1 mmol) in THF (22 mL) at −78 °C, under an atmosphere of N_2, by addition of

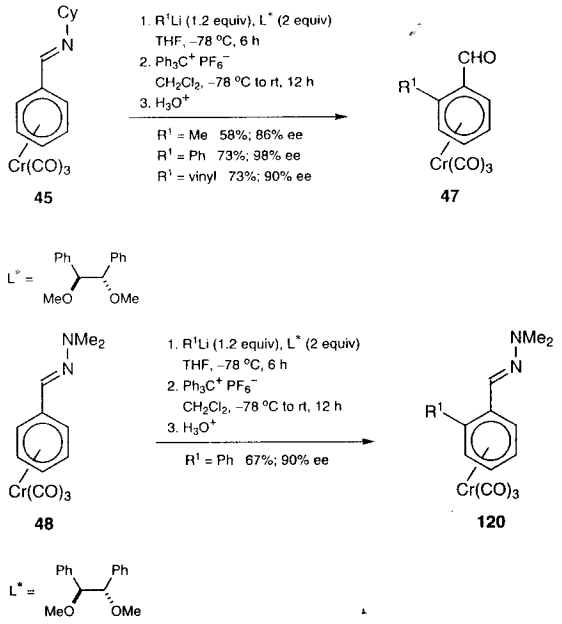
1.6 M BuLi in hexane (0.69 mL, 1.1 mmol), followed by warming at rt for 15 min. The resulting soln of the chiral base **114** was then cooled to −78 °C and TMSCl (0.38 mL, 3 mmol) added in one portion. A soln of [Cr(η⁶-anisole)$(CO)_3$] (**6**, M = Cr; R¹ = OMe; 248 mg; 1.0 mmol) in THF (3 mL), was then immediately added in one portion. After stirring at −78 °C for 30 min, sat. aq $NaHCO_3$ (5 mL) was added and the reaction allowed to warm to rt. The mixture was extracted with CH_2Cl_2 (40 mL), dried ($MgSO_4$), and the solvents evaporated. The resulting yellow oil was purified by flash column chromatography (silica gel, light petroleum ether/Et_2O 95:5), giving **117** as a yellow crystalline solid; yield: 264 mg (83%, 84% ee); mp 79–80 °C; $[\alpha]_D$ +205 (*c* 1.10, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{CO}$: 1957, 1898 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.32 (s, 9H), 3.74 (s, 3H), 4.78 (dd, 1H), 4.97 (d, 1H), 5.58 (d, 1H), 5.66 (dd, 1H). Determination of the ee was carried out by chiral HPLC [Chiracel OJ, hexane/EtOH 90:10, flow 1.5 mL·min^{-1}, detection 324 nm, retention time 4.35 min (major) and 6.68 min (minor)].

2.4.7.4 Variation 4: Diastereo- or Enantioselective Nucleophile Addition followed by *endo*-Hydride Abstraction

A conceptually different route to nonracemic planar chiral complexes is a sequence based on nucleophilic addition followed by *endo*-hydride abstraction.[121] This approach is successful with chromium–arene complexes bearing substituents (imines, hydrazones, oxazolines) that can coordinate the organolithium reagent. The diastereoselective version of these reactions used a (*S*)-1-amino-2-(methoxymethyl)pyrrolidine (SAMP) hydrazone complex, leading to diastereoselectivities in excess of 97%.[246] The enantioselective variant uses as nucleophile an alkyl- or aryllithium reagent (methyl-, butyl-, phenyl-, or vinyllithium) in the presence of the chiral ligand (spartein or diethers). Best results are reported for dimethoxydiphenylethane. The chiral nucleophile differentiates between the two enantiotopic *ortho* carbons. Hydride abstraction from the intermediate η⁵-cyclohexadienyl complex by the trityl cation, presumably again assisted by the Lewis basic aryl substituent, yields planar chiral complexes **47**, **119**, and **120** with enantioselectivities up to 98% (Scheme 41).[247]

Scheme 41 Enantioselective Nucleophile Addition/Hydride Abstraction[247]



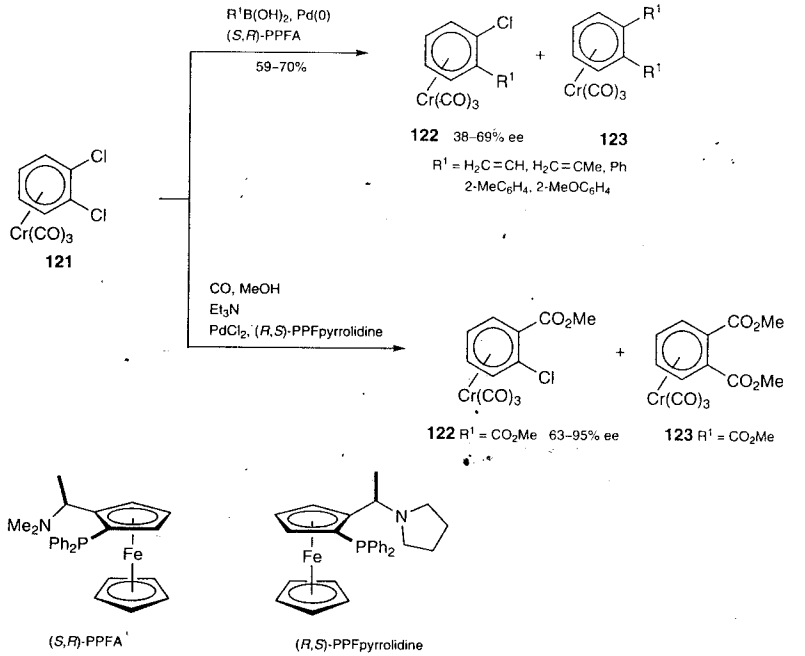


(1*R*)-Tricarbonyl(η⁶-2-vinylbenzaldehyde)chromium(0) (47, $R^1 = CH_2{=}CH$):[121,247]
1.6 M MeLi in THF (781 μL, 1.25 mmol) was added dropwise to a soln of tetravinylstannane (76 μL, 0.416 mmol) in THF (5.0 mL) at –78 °C. After stirring for 90 min, the solvent was removed in vacuo and the resulting white solid was dried for an additional 20 min. Toluene (11 mL) was added followed by (1*S*,2*S*)-dimethoxydiphenylethane (484 mg, 2.00 mmol). The mixture was stirred for 30 min, cooled to –78 °C, and complex **45** (0.32 g, 1 mmol) was added. The soln was allowed to stir for 6 h before the solvent was removed in vacuo. The red-brown, oily residue was dissolved in a minimum amount of dry CH_2Cl_2. The soln was cooled to –78 °C and a 0.4 M soln of Ph_3CPF_6 (0.85 g, 2.2 equiv) in CH_2Cl_2 (5.5 mL) was added quickly via syringe. The dark red mixture was allowed to warm to rt overnight, the volatiles were removed in vacuo and the black residue was dissolved in Et_2O (5.0 mL). Deoxygenated H_2O (5.0 mL) was added and the two-phase system was stirred vigorously at rt for 10 min. After separation of the phases, the organic phase was extracted with Et_2O (5 × 5 mL). The combined organic extracts were filtered over $MgSO_4$/Celite and the solvent was evaporated. The crude product was purified by flash column chromatography on (silica gel, gradient elution with hexane/Et_2O, 9:1 to 2:1). The product was isolated as a red oil; yield: 197 mg (74%, 90% ee); $[\alpha]_D$ –269 (*c* 0.11, $CHCl_3$); HPLC: Chiracel OD-H, hexane/iPrOH 80:20, 0.4 mL/min, major 33.7 min, minor 38.5 min; IR (toluene) $\tilde{\nu}_{CO}$: 1982, 1918 cm^{-1}; ^1H NMR (benzene-d_6, δ): 4.19 (d, 1H), 4.39 (d, 1H), 4.66 (dd, 1H), 4.99 (d, 1H), 5.11 (d, 1H), 5.43 (d, 1H), 6.59 (dd, 1H), 9.33 (s, 1H).

2.4.7.5 Variation 5: Palladium-Catalyzed Reactions

Syntheses of enantioenriched planar chiral chromium–arene complexes via palladium-catalyzed reactions have focused on the desymmetrization of tricarbonyl(1,2-dichlorobenzene)chromium (**121**). Suzuki coupling with alkenyl- and arylboronic acids, using a chiral phosphine ligand on palladium gives products **122** with enantioselectivities up to 69%.[248] The methoxycarbonylation of **121** gives an enantiomeric excess of about 60% (47% yield). Increasing reaction time affords a product of up to 95% ee, albeit in lower yield (31%). This has been shown to arise from a kinetic resolution in the formation of the bis-coupled product **123** ($R^1 = CO_2Me$),[379] (Scheme 42).

Scheme 42 Desymmetrization of Tricarbonyl(1,2-dichlorobenzene)chromium(0) by Suzuki Coupling[248]



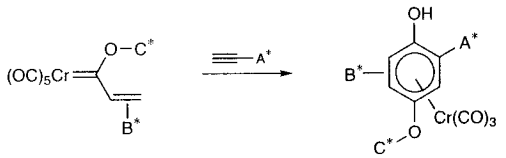
(1*S*,2*R*)-(–)-Tricarbonyl(η⁶-1-chloro-2-vinylbenzene)chromium(0) (122, $R^1 = CH{=}CH_2$); **General Procedure:**[248]
A soln of **121** (0.10 mmol), vinylboronic acid (0.30 mmol), $[\{Pd(\pi\text{-}C_3H_5)Cl\}_2]$ (0.005 mmol), the chiral phosphine ligand (*S*)-(*R*)-PPFA (**123**; 0.012 mmol), and 0.4 M TlOH [0.30 mmol in H_2O (0.75 mL)] in THF (1 mL) was degassed and stirred under argon at rt for 48 h. The mixture was quenched with H_2O and extracted with Et_2O. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography (silica gel, hexane/Et_2O 20:1) to provide the product as a yellow solid; yield: 59% (38% ee); mp 74 °C; $[\alpha]_D$ –110 (*c* 0.35, EtOH); HPLC: Chiracel OD, hexane/iPrOH 90:10, 0.5 mL·min^{-1}, minor 23.2 min, major 28.4 min; IR ($CHCl_3$) $\tilde{\nu}_{CO}$: 1980, 1900 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 5.12 (dd, 1H), 5.36 (dd, 1H), 5.45 (d, 1H), 5.50 (d, 1H), 5.70 (d, 1H), 5.74 (d, 1H), 6.77 (dd, 1H).

(1*S*,2*R*)-(+)-Tricarbonyl(η⁶-2-chloro-1,1′-biphenyl)chromium (122, **R = Ph**):
A similar reaction with **121**, $PhB(OH)_2$, and (*S*)-(*R*)-PPFA (**123**), stirring at 50 °C for 18 h, gave the product as a yellow oil; yield: 55% (69% ee; measured by HPLC after replacement of Cl by CO_2Me); $[\alpha]_D$ +42 (*c* 0.25, EtOH); IR ($CHCl_3$) $\tilde{\nu}_{CO}$: 1980, 1900 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 5.05–5.25 (m, 2H), 5.50–5.80 (m, 2H), 7.37–7.46 (m, 3H), 7.48–7.54 (m, 2H).

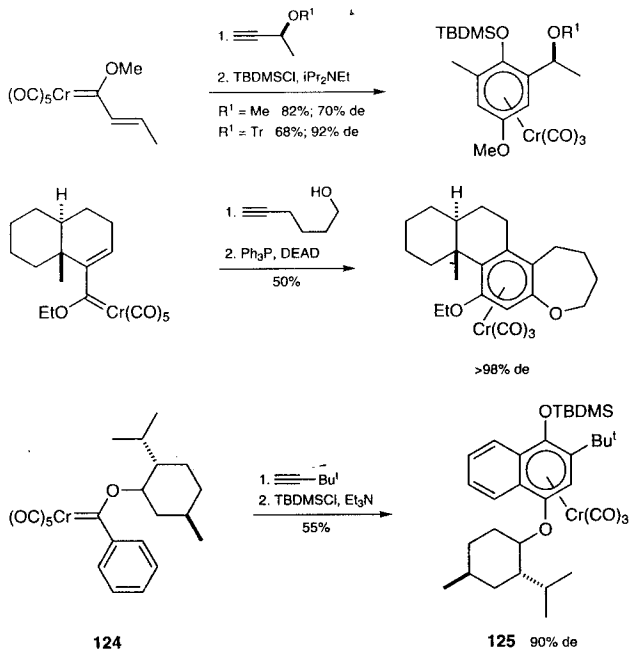
2.4.7.6 Variation 6: Diastereoselective Benzannulation Reactions

An alternative route to chiral nonracemic chromium–arene complexes is based on the benzannulation reaction of Fischer carbene complexes with alkynes, known as the Dötz reaction (see Section 2.4.4.3). Diastereoselective versions used a chiral alkyne (path A in Scheme 43),[249] a chiral auxiliary on the alkene part of the carbene (path B),[250,251] or a chiral auxiliary on the ether part of the carbene (path C).[252] Some examples are presented in Scheme 44. Good to excellent diastereoselectivities are obtained using a chiral alkyne (A*), or a chiral alkene (B*), although the last strategy (C*) is the most general. It allows easy variation of the alkyne and alkene groups with a chiral auxiliary that can be cleaved at the end of the sequence.

Scheme 43 Diastereoselectivity in the Dötz Annulation Reaction



Scheme 44 Selected Examples of the Dötz Annulation Reaction[249,250,252]



(1*R*,2*S*,5*R*)-(–)-[1–4,9,10-η⁶-2-*tert*-Butyl-1-(*tert*-butyldimethylsiloxy)-4-menthyloxynaphthalene]tricarbonylchromium(0) (125):[252]

A soln of the carbene complex **124** (0.874 g, 2 mmol) and *t*-BuC≡CH (0.975 mL, 8.0 mmol) in *t*-BuOMe (5 mL) was degassed and warmed to 55 °C for 55 min. After cooling to rt and filtration through silica gel, TBDMSCl (1.2 g, 8 mmol) and Et_3N (1.12 mL, 8 mmol) were added and the soln stirred at rt for 3 h. Solvent was removed under reduced pressure and the residue purified by column chromatography (petroleum ether/CH_2Cl_2 5:1, –10 °C) to give the product as a red solid; yield: 0.66 g (55%, 82% de); $[\alpha]_D$ +693 (*c* 0.90, $CHCl_3$); IR (petroleum ether) $\tilde{\nu}_{CO}$: 1958, 1890, 1877 cm^{-1}.

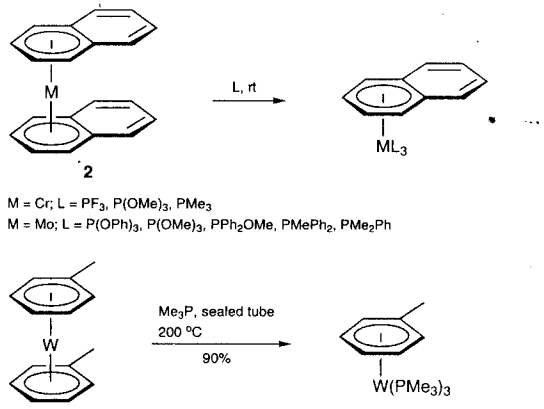
2.4.8 Method 8: Synthesis of [M(arene)(CO)$_x$(L)$_{3-x}$] Complexes

The most common routes to arene group 6 metal complexes with ligands other than carbonyl (e.g., phosphines, phosphites, alkenes, alkynes, amines, ethers, sulfides, nitriles, dihydrogen, dinitrogen) are arene substitution in bis(arene)metal complexes or carbonyl substitution in (arene)tricarbonylmetal complexes.

Arene sandwich complexes of group 6 metals are generally unreactive toward ligand substitution reactions. This is notably the case for bis(arene)chromium(0), whereas bis(arene)molybdenum(0) complexes are somewhat less robust and one arene ligand can be replaced by tertiary phosphines or by allyl chloride to give [Mo(arene)(PR^1_3)$_3$] and [{MoCl(η³-allyl)(η⁶-arene)}$_2$], respectively.[253,254] This route is also feasible for the tungsten complexes.[255] [Mo(arene)(PAr^1_3)$_3$] complexes can also be obtained directly by reduction of decachlorodimolybdenum with magnesium in the presence of arylphosphines.[256]

Sandwich complexes with condensed aromatic ligands, notably naphthalene, are much more labile. In both bis(naphthalene)chromium(0) (**2**, M = Cr) and bis(naphthalene)molybdenum (**2**, M = Mo), one naphthalene ligand is displaced readily by phosphines and phosphites to yield [M(naphthalene)L_3] complexes in good yield. Carbon monoxide and CNR^1 displace both naphthalene ligands to give homoleptic "ML_6" complexes. The initial step of metal—arene displacement involves slippage of the arene (haptotropic rearrangement), and in naphthalene complexes this is far easier than in the parent benzene complexes. Examples of [M(naphthalene)L_3] complexes prepared by this method are shown in Scheme 45.[14,16]

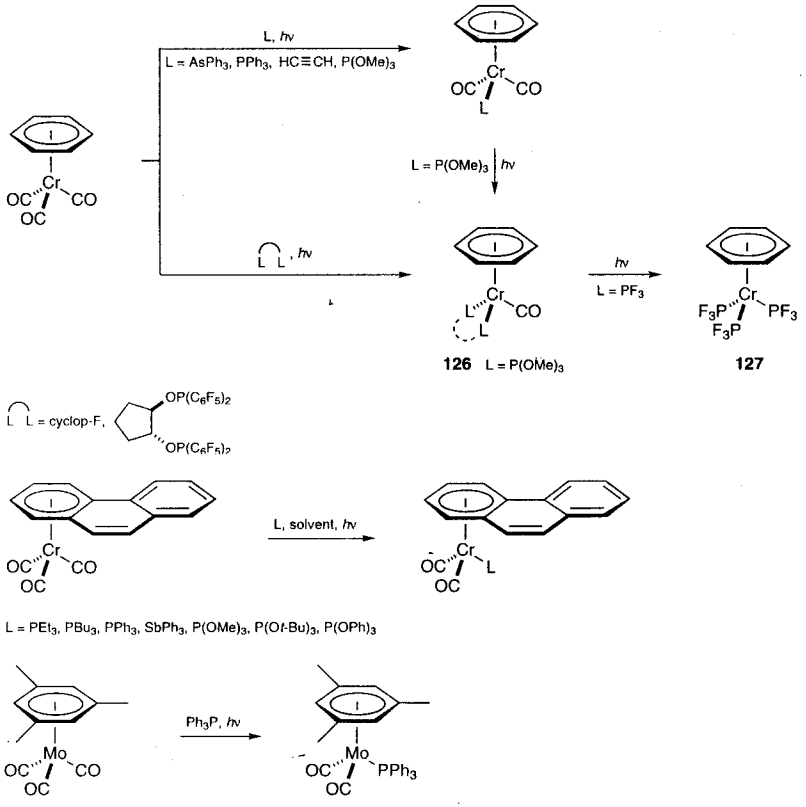
Scheme 45 Synthesis via Arene Displacement[14,16,255]



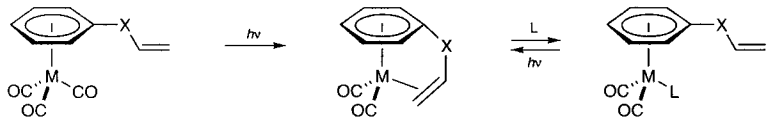
The vast majority of [M(η⁶-arene)$(CO)_{3-n}L_n$] complexes are derived from the corresponding [M(arene)$(CO)_3$] complexes by photolysis. Chromium complexes again provide the majority of examples. Irradiation (mercury lamp/Pyrex filter, halogen lamp) of (arene)tricarbonylchromium(0) complexes in the presence of an excess of an aryl- or alkylphosphine yields (arene)dicarbonyl(phosphine)chromium(0) complexes. The reaction stops at this stage because the stronger-donor phosphine ligand causes the remaining carbonyl ligands to be more tightly bound to the metal. Parallel observations are made with tetrahydrofuran, alkenes, and alkynes as entering ligands (Scheme 46). Exhaustive photolysis of (benzene)tricarbonylchromium(0) in the presence of an excess of trimethyl phosphite or trifluorophosphine leads to (benzene)(carbonyl)bis(triphenyl phosphite)chromium(0)

[**126**, L = $P(OMe)_3$] and to (benzene)tris(trifluorophosphine)chromium(0) (**127**, L = PF_3), respectively.[119] This reflects the weaker-donor/stronger-acceptor properties of these ligands compared to alkyl- or arylphosphines. Intramolecular reactions of ligand photosubstitution have also been studied intensively (Scheme 47). Chelation strongly stabilizes these alkene complexes compared to those containing an untethered alkene. Addition of phosphines results in the substitution of the alkene to afford [M(arene)$(CO)_2$L] complexes.

Scheme 46 Direct Photosubstitutions in (Benzene)tricarbonylchromium(0),[119,257–261] Tricarbonyl(phenanthrene)chromium(0),[262] and Tricarbonyl(1,3,5-trimethylbenzene)molybdenum(0)[263]



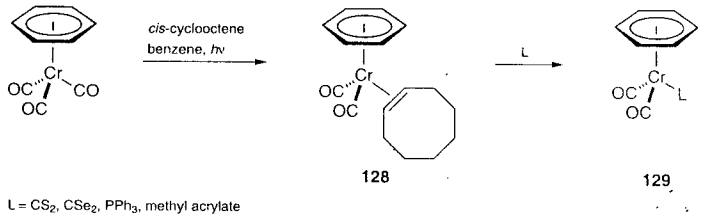
Scheme 47 Chelate Complexes: Alkene and Phosphorus Complexes[264,265]



Cyclooctene and tetrahydrofuran are labile ligands and are readily substituted in the dark by a variety of other ligands. This provides a two-step sequence to [Cr(arene)$(CO)_2$L] complexes that has a number of advantages over the direct method: it obviates the need for the use of an excess of the ligand, it is compatible with ligands that are sensitive to light,

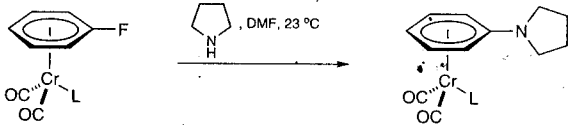
and it allows the introduction of precisely one new ligand. Examples are shown in Scheme 48.

Scheme 48 Substitution via Cyclooctene Complexes[266–269]



Ligands with different electronic and steric characteristics than carbonyl modify the physical properties and reactivity of the complexes.[270] Such modifications are used successfully in asymmetric catalysis of cross-coupling reactions[229] and in polymer synthesis.[271] Ligand modification has a large effect on the rate of *ipso* aromatic nucleophilic substitution (Scheme 49).

Scheme 49 Effect of Ligand Replacement on Nucleophilic Substitution Reactions[272]



L	$t_{1/2}$	Ref
PPh_3	>> 48 h	[272]
$P(OPh)_3$	6.1 h	[272]
tri(pyrrol-1-yl)phosphine	33.6 min	[272]
[benzyl(methyl)amino]di(pyrrol-1-yl)phosphine	1.5 min	[272]

These reactions are strictly stoichiometric at present because of the high activation barrier for arene exchange. A step toward a solution is the finding that the acrylate complex **130** readily exchanges the arene at room temperature. This occurs presumably by the mechanism shown in Scheme 50.[268] This concept of replacing one carbonyl ligand in the "$Cr(CO)_3$" group by a ligand capable of reversibly adopting a bidentate binding mode and thereby labilizing the metal—arene bond has seen further development. Arene exchange for benzene-d_6 (Table 1) is considerably more facile in the complexes **131** than in the corresponding "$Cr(CO)_3$" complex (see Section 2.4.4.3).[380]

Scheme 50 Arene Exchange under Mild Conditions via Ligand Modification in the "$Cr(CO)_3$" Group[268,380]

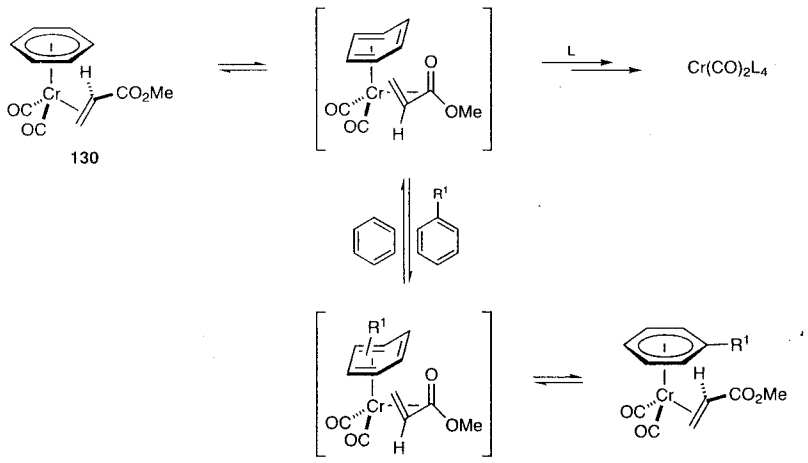
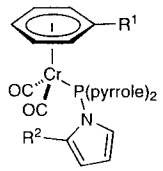


Table 1 Arene Exchange[380]

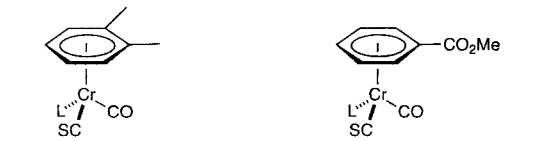


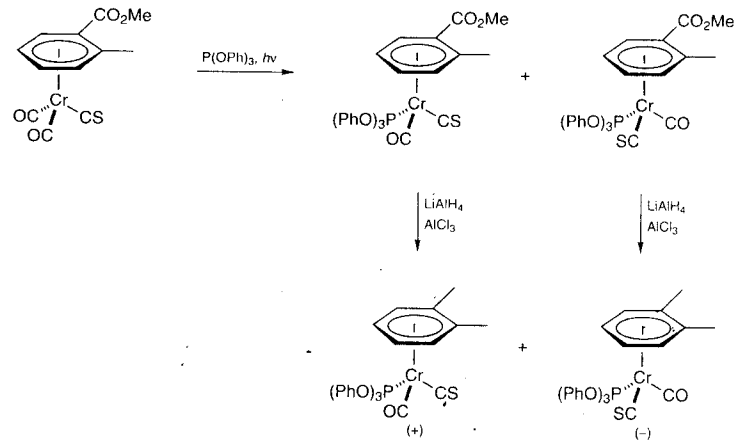
131

R^1	R^2	$t_{1/2}$	Reaction Temp (°C)	Arene	Ref
F	H	> 16 h	150	benzene-d_6	[380]
F	SMe	0.7 h	60	benzene-d_6	[380]
F	SMe	2 h	80	benzene-d_6	[380]
F	CO_2Me	0.5 h	70	benzene-d_6	[380]

Carbonyl substitution also gives access to chiral complexes, either by introduction of a chiral ligand on the metal,[261] or by a stepwise substitution of two carbonyl ligands, leading to a chiral metal center.[273] No asymmetric induction is observed in the second carbonyl displacement but chiral complexes have been resolved via chromatographic separation of the mixture of diastereoisomers before reduction and hydrogenolysis. Examples are shown in Scheme 51.

Scheme 51 Examples of Complexes with a Chiral Chromium Atom[273]





(η^6-Benzene)dicarbonyl(η^2-methyl acrylate)chromium(0) (129, $L^1 = CH_2{=}CHAc$):[268]

(η^6-Benzene)dicarbonyl(η^2-*cis*-cyclooctene)chromium(0) (128); **Typical Procedure:**[267]

Benzene (ca. 250 mL) was distilled under N_2 from sodium/benzophenone into a Pyrex UV irradiation vessel (capacity 350 mL) fitted with a water-cooled quartz finger containing a 100-W Hanovia high-pressure Hg lamp. $[Cr(CO)_3(C_6H_6)]$ (1.0 g, 4.7 mmol) and excess *cis*-cyclooctene (50 mL, 340 mmol) were added. The reaction vessel was wrapped in aluminum foil and placed in an ice–water bath, and the UV lamp was turned on.

CAUTION: *Exposure of the eyes to UV light must be avoided at all times.*

Throughout the reaction, a flow of N_2 was passed through the mixture. On irradiation, the color of the soln gradually turned dark red owing to the formation of the cyclooctene complex. The progress of the reaction was conveniently monitored by diluting a small sample in an equal volume of hexane and observing the IR spectra (CO bands, 1970 and 1900 cm^{-1} for starting material, then 1900 and 1850 cm^{-1} for the cyclooctene complex). After 2.5 h, the reaction was complete; the mixture was allowed to stand 30 min under a steady stream of N_2 in order to remove any remaining CO.

(η^6-Benzene)dicarbonyl(η^2-methyl acrylate)chromium(0) (129, $L^1 = CH_2{=}CHAc$):[268]

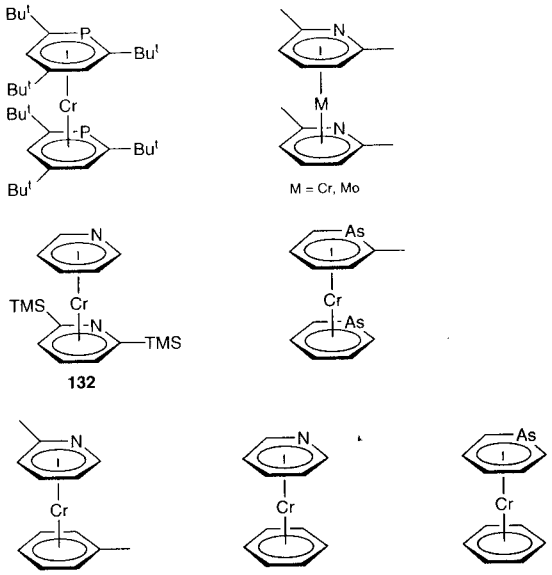
On completion of the above irradiation, methyl acrylate (0.43 mL, 4.7 mmol, 1 equiv) was added to the mixture. After 16 h the mixture was filtered over Celite and the volatiles were removed in vacuo. The residue was dissolved in hexane/benzene (20:1) and recrystallized at –40 °C to give red-orange crystals of the product; yield: 0.92 g (72%); mp 82–83 °C; IR (hexane) $\tilde{\nu}_{CO}$: 1948, 1896, 1704 cm^{-1}.

2.4.9 Method 9: Synthesis of Heteroarene Complexes

Heteroarene complexes (see Scheme 52) can be divided into two main categories: bis(arene)metal complexes and $[M(arene)L_3]$ complexes. As in the case of benzene-derived sandwich complexes, the most common synthetic method is the direct reaction of the ligand with metal vapor. This was used for series of chromium and molybdenum complexes. Displacement of an arene ring in bis(2,6-dimethylpyridine)molybdenum(0) with phosphines affords $[Mo(2,6\text{-dimethylpyridine})L_3]$ ($L = PMe_3$, PPh_2H, $PPhMe_2$).[274] The unsubstituted bis(pyridine)chromium(0) complex is obtained via desilylation of complex **132**. Bis(borabenzene)chromium complexes are synthesized by reaction of $K[C_5H_5BR^1]$

(R^1 = Me, Ph) with chromium(III) chloride or the chromium(II) chloride–tetrahydrofuran complex.[275] Mixed complexes could also be obtained via the same synthetic route. Competition experiments demonstrate that heteroaromatic rings are better ligands than benzene derivatives.

Scheme 52 Heteroarene Sandwich Complexes[276–280]



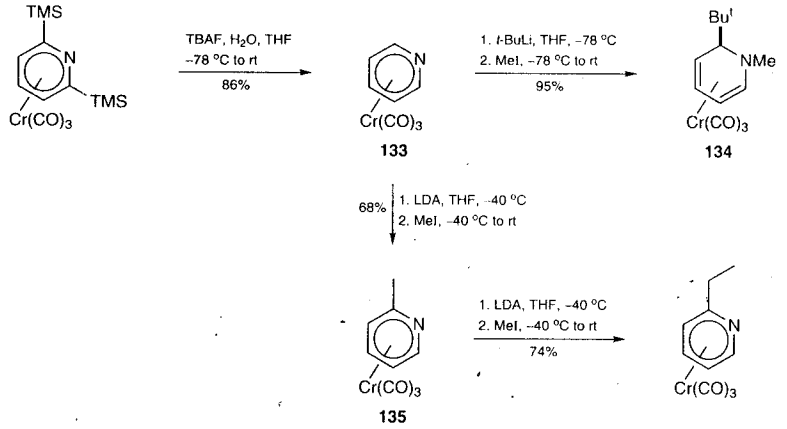
There are few examples of [M(heteroarene)L_3] complexes. They can be divided into two categories: η^6-complexes such as the pyridine, phosphabenzene, arsabenzene, and borabenzene derivatives; and η^5-complexes with pyrrole, thiophene, and selenophene ligands.

Pyridines form σ-coordination complexes with chromium(0), e.g. [$Cr(CO)_3$(pyridine)$_3$]. Coordination to the π-system is feasible with 2,6-disubstituted pyridines.[281–283] Although sterically hindered, the nitrogen lone pair in these complexes retains its capacity to form adducts with Lewis acids.[283,284] The reaction of 4-vinylpyridine with [$M(CO)_6$] or [$M(CO)_3$-$(NCMe)_3$] results in the η^6-complex.[285]

It is interesting to note that the preference of unsubstituted pyridine for σ-complexation may also be due to electronic reasons. Heilbronner et al. showed that the HOMO orbital of pyridine is localized on nitrogen and has σ-character, whereas in 2-substituted or 2,6-disubstituted pyridines the HOMO is a π-orbital.[286]

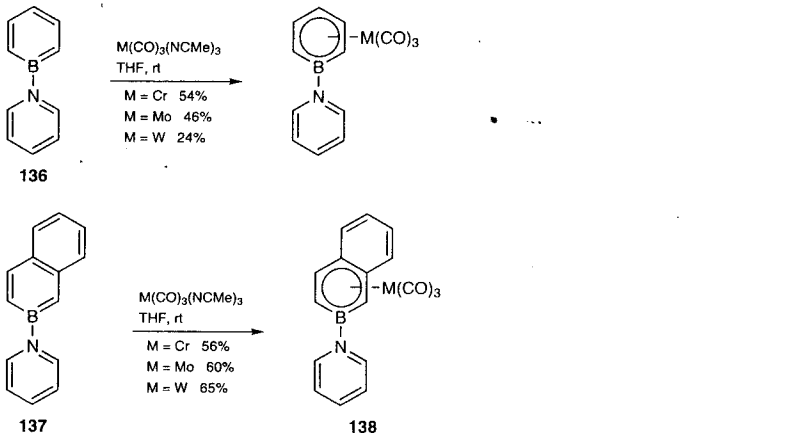
Pyridine ligands are more labile than naphthalene in arene exchange reactions (rates measured with toluene as entering ligand).[79] In contrast, 2,6-dimethylpyridine is less labile than naphthalene versus ligands such as trimethyl phosphite.[287] Complexation of 1,6-bis(trimethylsilyl)pyridine followed by desilylation with fluoride ion gives the unsubstituted pyridine complex **133** (Scheme 53).[288,289] Nucleophilic attack followed by electrophilic quench with methyl iodide leads to the N-methylated η^4-complex **134**. Lithiation with lithium diisopropylamide followed by electrophilic quench leads to the 2-substituted complex **135**. Deprotonation in the benzylic position is preferred over ring lithiation.[290,291] Dicarbonyl(η^6-2,6-dimethylpyridine)(triphenylphosphine)chromium(0) can be obtained by photochemical reaction on the tricarbonyl complex. The phosphine compound is thermally more stable than the tricarbonylchromium analogue. It also does not readily undergo arene exchange reactions.[292]

Scheme 53 Reactions of Pyridine Complexes[288–291]



Borabenzene complexes are scarce. Herberich et al. synthesized tricarbonyl(1-methylborinato)chromium using tris(ammine)tricarbonylchromium(0).[293] Complexation of 1-(borinin-1-yl)pyridine (**136**) and 1-(2-benzoborinin-2-yl)pyridine (**137**) with [$M(CO)_3(MeCN)_3$] (M = Cr, Mo, W) at room temperature demonstrated that the aromatic ring containing the boron atom is the better ligand (Scheme 54).[294] Fu and co-workers showed that the (borabenzene)tricarbonylchromium(0)–tetrahydrofuran complex has Lewis acid properties and complexes acroleins, leading to a species where the arene ring is coplanar with the acrolein plane.[295] Using a borabenzene Lewis acid–chiral base couple, the first planar chiral borabenzene complex was obtained with very high diastereoselectivity.[226]

Scheme 54 Complexation of Boron-Containing Arenes[294]



The first phosphabenzene complexes were obtained by direct complexation of 2,4,6-triphenylphosphorin using hexacarbonylmetal complexes (M = Cr, Mo, W) in dibutyl ether.[296–298] The "$M(CO)_3$" fragment coordinates the heteroarene ring exclusively, which is in contrast to the reactivity of the analogous pyridine ligand.[299] The molybdenum complex could also be synthesized by arene exchange using tricarbonyl(mesitylene)molybdenum(0).[300] Like pyridine complexes, borabenzene complexes undergo sequential nucleophile/electrophile addition reactions to yield η^5-λ^5-complexes. The "$Cr(CO)_3$" moiety can be removed by addition of pyridine.[301] Only bulky substituents in the 2,6-positions prevent η^1-coordination (see review on phosphorus heteroarenes[302]). Arsabenzene com-

plexes of chromium, molybdenum, and tungsten are synthesized using $[M(CO)_3(NCMe)_3]$. Their properties resemble those of the phosphorus analogues.[303]

1,3-Diphosphabenzene[304] and 1,2,5-triphosphabenzene complexes[305] are prepared by trimerization reactions. 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene displaces the arene in $[M(CO)_3(toluene)]$ (M = Mo, W) in tetrahydrofuran at room temperature.[306] There is also one example of a tricarbonyl(η^5-1,2,4-triphosphole)metal complex (M = Cr, Mo, W).[307]

Tricarbonyl(thiophene)chromium(0) complexes have been known for 40 years and are easily synthesized, either by direct thermolysis of hexacarbonylchromium(0) in dibutyl ether,[308,309] or by reaction with tris(acetonitrile)tricarbonylchromium(0),[310] tris(ammine)tricarbonylchromium(0),[62] tricarbonyltris(γ-picoline)chromium(0) and boron trifluoride,[311,312] or tricarbonyl(naphthalene)chromium(0).[313] A diastereoselective complexation of a 2,3-disubstituted thiophene bearing a chiral alcohol substituent in the 2-position was realized with tris(acetonitrile)tricarbonylchromium(0) at room temperature in dioxane, leading to 85% de.[314] There are but few investigations of the reactivity of these compounds. Lithiation occurs preferentially at the 2-position.[315–318] Addition of the lithiated complex to aldehydes has been reported.[313] Analogous molybdenum and tungsten complexes have not been documented, although theoretical studies predict the molybdenum complex to be stable.[319] Synthesis of tricarbonyl(selenophene)chromium(0) was achieved by reaction of selenophene with hexacarbonylchromium(0).[320]

Tricarbonyl(pyrrole)chromium(0) complexes are documented, though their access is not as straightforward as that of the thiophene analogues. Direct complexation with hexacarbonylchromium(0) gives poor results, though with *N*-methylpyrrole the situation is improved (to 46%).[321] The use of tris(acetonitrile)tricarbonylchromium(0)[321] or tetracarbonyl(norbornadiene)chromium(0)[322] is more successful, and 1-methyl-, 1,2,5-trimethyl-, and 1,2,3,4,5-pentamethylpyrrole tricarbonylchromium complexes have been obtained by this route. It is interesting to note that, in the case of 2,5-dimethyl-1-phenylpyrrole, heterocycle complexation is kinetically preferred [tris(acetonitrile)tricarbonylchromium(0), 60 °C], whereas the phenyl ring only is complexed under thermodynamic conditions [hexacarbonylchromium(0), 150 °C].[321] Tricarbonyl(1-methylpyrrole)chromium(0) can be used as a "$Cr(CO)_3$" transfer reagent in arene exchange reactions to give access to η^6-arene complexes that are difficult to synthesize by other methods[83] (see Section 2.4.4.3).

[(η^6-1-(2-Benzoborinin-2-yl)pyridine]tricarbonylchromium(0) (138, M = Cr); General Procedure:[294]

All manipulations were carried out under an inert atmosphere using degassed solvents. A suspension of $[Cr(CO)_3(NCMe)_3]$ (1.6 mmol) and 1-(2-benzoborinin-2-yl)pyridine (**137**, 1.5 mmol) was stirred in dioxane (10 mL) at rt. The mixture was concentrated to 5 mL and hexane (15 mL) added to precipitate the product. The precipitate was filtered, washed with a small quantity of hexane, dried under vacuum, and recrystallized from CH_2Cl_2 (4 mL) to give a red solid; yield: 56%; mp 209 °C; IR (KBr) $\tilde{\nu}_{CO}$: 1925, 1833, 1796 cm^{-1}; ^1H NMR (CD_2Cl_2, δ): 4.74 (dd, 1H), 5.14 (d, 1H), 6.49 (d, 1H), 7.16 (dd, 1H), 7.31 (dd, 1H), 7.42 (d, 1H), 7.67 (d, 1H), 7.94 (t, 2H), 8.35 (t, 1H), 9.05 (d, 2H); ^{11}B NMR (CD_2Cl_2, δ): 23.1.

Similarly was prepared [(η^6-1-(2-benzoborinin-2-yl)pyridine]tricarbonylmolybdenum(0) (**138**, M = Mo), except that the product precipitated from the reaction after 16 h and no concentration was necessary; yield: 60%; orange solid; mp 215 °C; IR (KBr) $\tilde{\nu}_{CO}$: 1925, 1835, 1800 cm^{-1}; ^1H NMR (CD_2Cl_2, δ): 5.19 (dd, 1H), 5.42 (d, 1H), 6.80 (d, 1H), 7.10 (dd, 1H), 7.29 (dd, 1H), 7.45 (d, 1H), 7.64 (d, 1H), 7.93 (t, 2H), 8.35 (t, 1H), 9.02 (d, 2H); ^{11}B NMR (CD_2Cl_2, δ): 26.8.

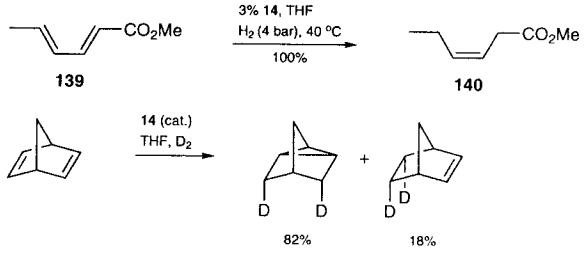
Also similarly prepared was [(η^6-1-(2-benzoborinin-2-yl)pyridine]tricarbonyltungsten(0) (**138**, M = W), where again the product precipitated from the reaction after 16 h and no concentration was necessary: yield: 65%; orange solid; mp 244 °C; IR (KBr) $\tilde{\nu}_{CO}$: 1955, 1820, 1796 cm^{-1}; ^1H NMR (CD_2Cl_2, δ): 5.04 (dd, 1H), 5.42 (d, 1H), 6.60 (d, 1H), 7.09 (dd, 1H), 7.22 (dd, 1H), 7.43 (d, 1H), 7.56 (d, 1H), 7.94 (t, 2H), 8.36 (t, 1H), 8.98 (d, 2H); ^{11}B NMR (CD_2Cl_2, δ): 24.2.

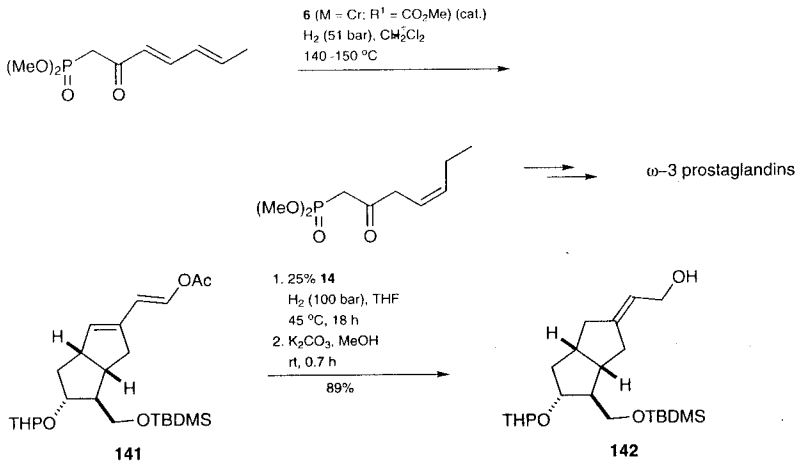
Applications of Product Class 4 in Organic Synthesis

2.4.10 Method 10: (Arene)tricarbonylchromium(0) Complexes as Catalysts

(Arene)tricarbonylchromium(0) complexes catalyze the 1,4-addition of hydrogen to 1,3-dienes, the hydrogenation of alkynes to *Z*-alkenes, and the isomerization of 1,4- and 1,3-dienes.[323,324] The high chemo-, regio-, and stereoselectivity of these processes make them powerful synthetic tools. All of these processes involve metal—arene bond cleavage to generate the catalytically active species $[Cr(CO)_3S_3]$ (S = solvent). The most active precatalysts are therefore complexes that undergo arene displacement readily, such as tricarbonyl(naphthalene)chromium(0) (**14**). Coordinating solvents (tetrahydrofuran, acetone) are best and, in tetrahydrofuran, 1,4-hydrogenation of dienes occurs slowly already at ambient temperature and ambient pressure, although slight warming (50 °C) and higher pressure (40–100 bar) render the process more efficient. Tricarbonyl(methyl benzoate)chromium(0) (**6**, M = Cr; $R^1 \doteq CO_2Me$) is used at ca. 120 °C and has a longer induction period. The hydrogenation reaction likely involves a $[Cr(H_2)(CO)_3(diene)]$ complex in which the diene adopts an *s-cis* conformation.[325] In the absence of hydrogen, isomerization of the diene via 1,5-hydrogen migration takes place to form the most stable diene capable of adopting a cisoid conformation.[324,326] This process, as well as that of isomerization of 1,4-dienes to 1,3-dienes, presumably occurs via $[CrH(CO)_3(pentadienyl)]$ intermediates.[327,328] 1,4-Hydrogenation of 1,3-dienes has been applied in prostaglandin[329] and in pheromone syntheses.[330] Examples shown in Scheme 55 include the hydrogenation of methyl sorbate (**139**) to methyl (*Z*)-hex-3-enoate (**140**),[323] the 1,5-addition of hydrogen and C—C bond formation in norbornadiene,[331] the tricarbonyl(methyl benzoate)chromium(0) (**6**, M = Cr; $R^1 = CO_2Me$) catalyzed synthesis of a key reagent in the synthesis of ω–3 prostaglandins,[329] and the stereocontrol of the exocyclic alkene in a key intermediate **142** of a prostacyclin analogue.[332] (Arene)tricarbonylmolybdenum(0) and (arene)tricarbonyltungsten(0) complexes give products of low regio- and stereoselectivity in this transformation, and ligand substitution in the tricarbonylchromium group often leads to loss of activity. One exception to this is the methyl acrylate complex **130**.[268]

Scheme 55 (Arene)tricarbonylchromium(0) Complexes as Hydrogenation Catalysts of 1,3-Dienes[323,329,331,332]

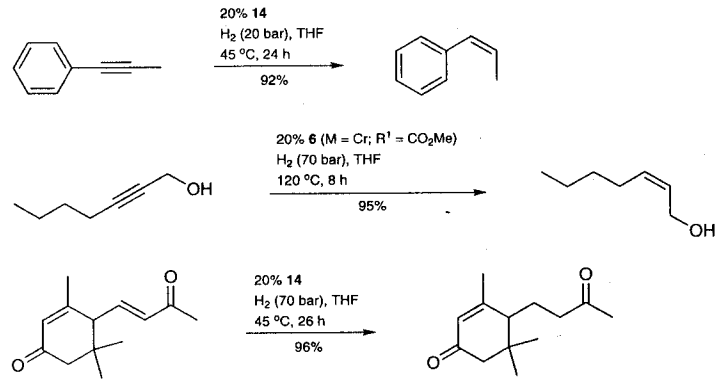




141 142

Other unsaturated functional groups that are hydrogenated to Z-alkenes by (arene)tricarbonylchromium(0) complexes are enones capable of adopting a cisoid conformation and alkynes (Scheme 56).[333]

Scheme 56 (Arene)tricarbonylchromium(0) Complexes as Hydrogenation Catalysts of Alkynes and Enones[333]



(Arene)tricarbonylchromium(0) complexes also catalyze the addition of carbon tetrachloride to alkenes[334] and the dehydrohalogenation of alkyl halides.[335] Tricarbonyl(naphthalene)chromium(0) (**14**) catalyzes the [6π + 2π]-cycloaddition reaction between cycloheptatriene and ethyl acrylate.[336,337]

(Arene)tricarbonylchromium(0) complexes are also photoinitiators for the radical polymerization of acrylates[338,339] in the presence of carbon tetrachloride. This process presumably is initiated by a photolytic carbonyl–acrylate exchange followed by arene dissociation (see Section 2.4.8).

(1*S*,5*S*,6*S*,7*R*)-6-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-(*E*)-3-(2-hydroxyethylidene)-7-[(tetrahydropyranyl)oxy]bicyclo[3.3.0]octane (142):[332]

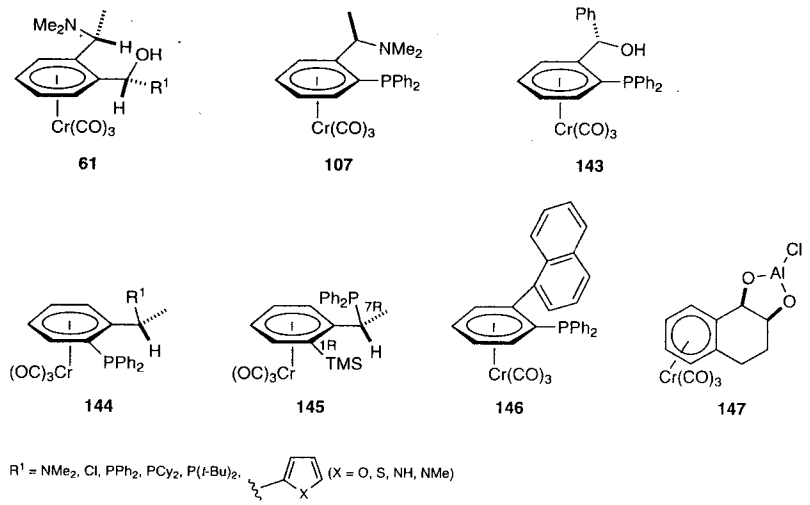
The dienol acetate **141** (123 mg, 0.28 mmol) and [Cr(CO)$_3$(naphthalene)] (**14**; 22 mg, 0.08 mmol) were dissolved in THF (10 mL). After strict deoxygenation by three freeze–pump–thaw cycles, the soln was heated at 45 °C with stirring under an atmosphere of H_2 (100 bar pressure) for 18 h and concentrated. The product was purified by column chromatography (silica gel, Et$_2$O/hexane 1:5) to give the allylic acetate (110 mg, 89%) as a colorless oil. To a stirred soln of the acetate (110 mg, 0.25 mmol) in MeOH (0.3 mL) was added anhyd K_2CO_3 (69 mg, 0.5 mmol) at rt and the resulting suspension was stirred at rt for 40 min and concentrated. The residue was purified by column chromatography (silica gel, Et$_2$O) to afford **142** as a colorless oil; yield: 99 mg (89%); ^{1}H NMR ($CDCl_3$, δ): 0.04 (s, 6H), 0.90 (s, 9H), 4.05 (d, J = 6 Hz, 2H), 4.55 (m, 1H), 5.46 (br t, J = 6.8 Hz, 1H).

2.4.11 Method 11: (Arene)tricarbonylchromium(0) Complexes as Auxiliaries and Building Blocks

2.4.11.1 Variation 1: (Arene)tricarbonylchromium(0) Complexes as Chiral Ligands

Following the wide success of ferrocene-derived planar chiral ligands[228] and the rapid development of enantioselective and diastereoselective methodologies in the field of (arene)tricarbonylchromium(0) complexes (see Section 2.4.7), it was only a matter of time before attention was directed to chiral ligands based on this group.[199] A limitation in their application is noted in as far that the chromium—aryl bond is less robust that the Fe—Cp bond. The general synthetic routes to nonracemic planar chiral ligands of this class of compounds have been those outlined in Section 2.4.7, with the first syntheses based on (*S*)-α-methylbenzylamine derivatives (see Scheme 39). Examples of nonracemic planar chiral mono- and bidentate ligands are shown in Scheme 57 and include complexes **63** (synthesis in Scheme 15),[156] **107** (R^1 = PPh$_2$) (synthesis in Scheme 39),[229] **143** (prepared by enantioselective lithiation of the tricarbonylchromium(0) complex of triphenylphosphine oxide),[340] **144**,[341] **145**,[232] and **146**.[342] Ligand **145** was synthesized by reacting *ent*-**108** (see Scheme 37) with lithium diphenylphosphide, and ligand **146** was obtained by enantioselective lithiation–bromination of the carbamate complex **118** (Scheme 40), Suzuki coupling, and nucleophilic substitution. Complex **107** serves as a convenient starting material for the wide range of ligands listed under structure **144**.[341,381,382]

Scheme 57 Nonracemic Ligands Based on Planar Chiral (Arene)tricarbonylchromium(0) Complexes[156,229,232,340–342]

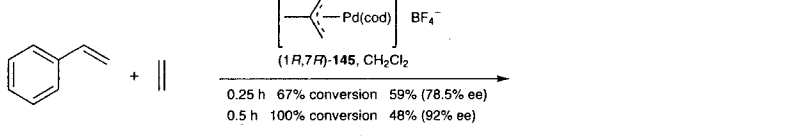


61 107 143 144 145 146 147

The ligands **61** were used successfully in the enantioselective addition of diethylzinc(II) to benzaldehyde.[156] Ligand **107** (R^1 = PPh$_2$) gave a 61% ee in the palladium-catalyzed cross-

coupling reaction between (1-phenylethyl)zinc(II) chloride and vinyl bromide.[343] Ligands **143** and **145** were applied to the palladium-catalyzed allylic substitution of 1,3-diphenylacetoxypropene with dimethyl sodiomalonate to give the substitution product in 86% ee (at −78 °C) and 92% ee (at room temperature), respectively.[341,342] Ligands **144** ($R^1 = PPh_2$, PCy_2), like the corresponding ferrocene derivatives, were used highly successfully in asymmetric rhodium catalyzed sulfonation reactions.[381] Asymmetric inductions with the more bulky ligand **144** [$R^1 = P(t\text{-}Bu)_2$] was poor. Iridium-catalyzed hydroamination of alkenes with **144** ($R^1 = PPh_2$, PCy_2) gave moderate enantioselectivities.[381] Asymmetric palladium-catalyzed hydrosilylation of styrenes proceeded particularly well with ligands **144** (R^1 = 2-furyl, 2-thiophenyl). Enantioselectivity in this transformation is in the 80–90% range.[382] The palladium-catalyzed enantioselective hydrovinylation of styrene to give 3-phenylbut-1-ene (**148**) proved highly efficient in the presence of ligand **145**, although isomerization (with kinetic resolution) of 3-phenylbut-1-ene to 2-phenylbut-2-ene is a competitive side reaction (Scheme 58).[232]

Scheme 58 Palladium-Catalyzed Asymmetric Hydrovinylation of Styrene[232]



148

The in situ prepared planar chiral Lewis acid **147** catalyzes the asymmetric Diels–Alder reaction between cyclopentadiene and acroleins (up to 95% ee).[383]

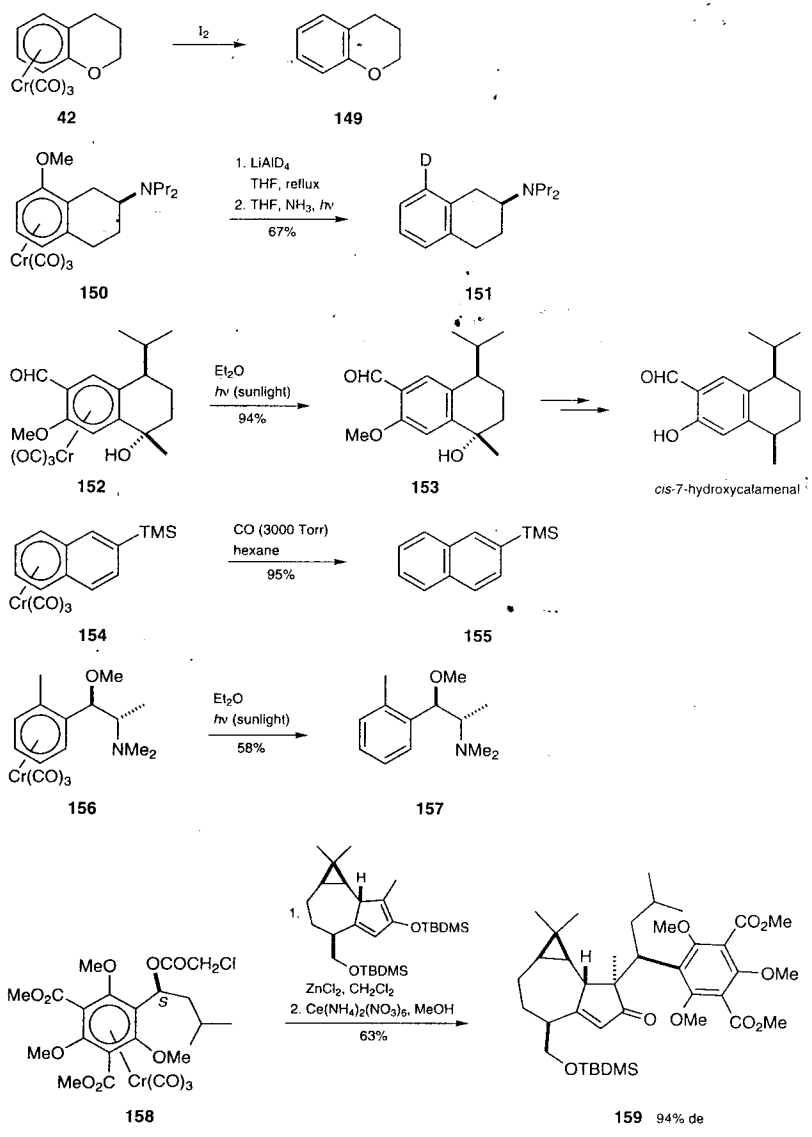
(*S*)-3-Phenylbut-1-ene (148); General Procedure:[232]

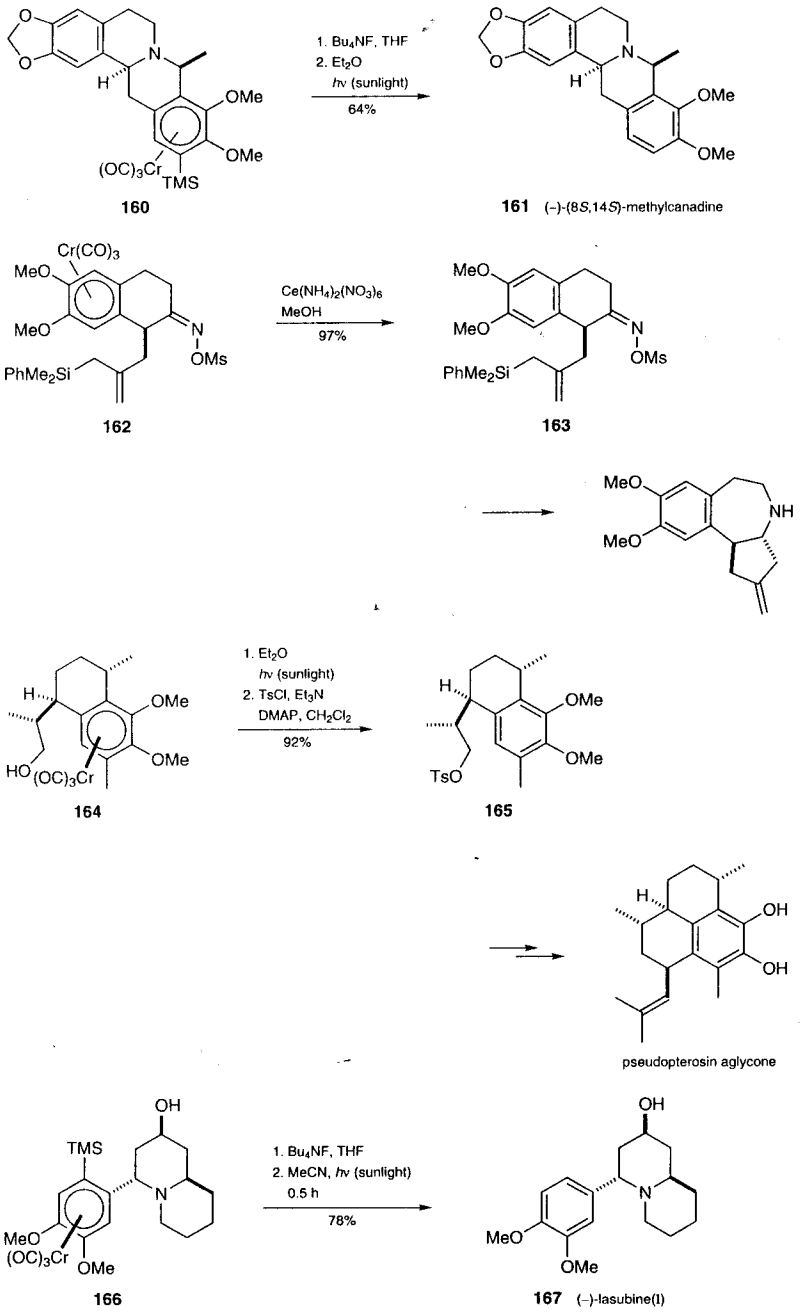
A soln of ligand (1*R*,7*R*)-**145** (0.05 mmol) in CH_2Cl_2 was added to a soln of [Pd(η^3-C_4H_7)(η^4-cycloocta-1,5-diene)]BF_4[344] (0.05 mmol) in CH_2Cl_2. The mixture (20 mL) was stirred for 60 min at 0 °C and then transferred via a syringe with a stainless-steel cannula into a 75-mL steel autoclave equipped with a magnetic stirring bar. The autoclave was cooled with an ice bath. Chilled styrene (4 mL, 34.8 mmol; distilled from CaH_2 under argon) was added and the autoclave was pressurized with ethene (22.5 × 10^3 Torr initial pressure, 99.5% purity). The reaction was carried out over a period of 15 min or 30 min at rt. After the reaction, the autoclave was slowly vented and the mixture separated from the catalyst by flash chromatography over basic alumina. The products were analyzed by chiral GC (Lipodex E column). The 15 min reaction afforded (*S*)-3-phenylbut-1-ene; yield: 59% (78.5% ee); also produced were styrene (33%), and (*E*)- and (*Z*)-2-phenylbut-2-ene (3.2%). The 30 min reaction (at 100% conversion) also gave (*S*)-3-phenylbut-1-ene; yield: 48% (92% ee); (*E*)- and (*Z*)-2-phenylbut-2-ene were also produced (50%).

2.4.11.2 Variation 2: Arene Decomplexation

The regio- and stereoselective transformations of arenes that are possible by temporary complexation of the tricarbonylchromium group have led to extensive applications, with efficient product decomplexation being an important step in the sequence. The metal—arene bond is readily cleaved upon oxidation of the metal [cerium(IV), iron(III), iodine, *hν*/oxygen]. The mildest procedure is the exposure of a solution of the complex in diethyl ether or acetonitrile to sunlight and air for a few hours. This allows the isolation of the arene in yields that are often >80%. Refluxing of an (arene)tricarbonylchromium(0) complex in pyridine cleaves the metal—arene bond and allows recycling of the chromium(0) complex in the form of tricarbonyltris(pyridine)chromium(0);[345] in tricarbonyl(naphthalene)chromium(0) (**14**) and substituted derivatives the metal—arene bond is readily cleaved by stirring the complex under an atmosphere of carbon monoxide or by applying pressure.[78] Scheme 59 lists a number of examples of decomplexation reactions and the key transformations used in the synthesis of the complexed products.[346–351]

Scheme 59 Cleavage of the Chromium–Arene Bond[346–351]



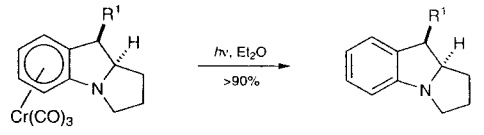


160 **161** (–)-(8*S*,14*S*)-methylcanadine

162 **163**

164 **165**

166 **167** (–)-lasubine(I)



168 **169**

R^1 = CH_2OH, Me, $(CH_2)_2OH$, Et, Bn

Key Transformation	Complex	Decomplexation Method, Solvent	Product	Yield (%)	Ref
nucleophilic substitution (Section 2.4.5.2, Scheme 8)	**42**	I_2, Et_2O	**149**	–	[115]
nucleophilic substitution (Section 2.4.5.2)	**150**	hν, THF/NH_3	**151**	67%	[346]
lithiation + formylation (Section 2.4.5.1) stereoselective nucleophilic addition to ketone (Section 2.4.6.1)	**152**	hν (sunlight), Et_2O	**153**	94%	[347]
regioselective lithiation + trapping with TMSCl (Section 2.4.5.1)	**154**	CO, 3000 Torr, hexane	**155**	95%	[78]
diastereoselective lithiation + trapping with MeI	**156**	hν (sunlight), Et_2O	**157**	58%	[348]
nucleophilic addition to benzylic carbocation (Section 2.4.6.2)	**158**	$Ce(NH_4)_2(NO_3)_6$, MeOH	**159**	63%	[349]
diastereoselective benzylic alkylation of *endo*-**17** (Section 2.4.6.3, Scheme 4)	**160**	hν (sunlight), Et_2O	**161**	64%	[61]
diastereoselective reactions at the benzylic positions	**162**	$Ce(NH_4)_2(NO_3)_6$, MeOH	**163**	97%	[350]
diastereoselective alkylation	**164**	hν, Et_2O	**165**	92%	[351]
diastereoselective aza Diels–Alder reaction, radical cyclization (Section 2.4.6.4, Scheme 31)	**166**	hν (sunlight), MeCN	**167**	84%	[195]
complexation of indene derivative, diastereoselective reduction, diastereoselective alkylation	**168**	hν, Et_2O	**169**	>90%	[384]

(–)-Lasubine(I) (167):[195]

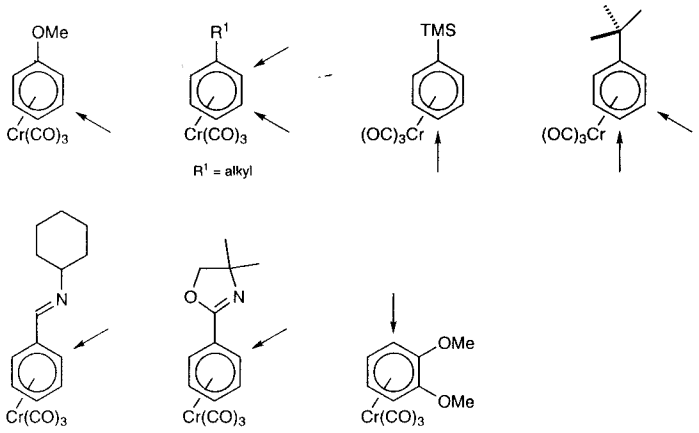
To a stirred soln of complex (–)-**166** (200 mg, 0.400 mmol) in THF (5 mL) at –78 °C, was added a 1 M TBAF soln in THF (0.44 mL, 0.44 mmol, 1.1 equiv). Stirring was continued for 30 min followed by extraction (Et_2O/H_2O). Column chromatography gave the desilylated complex (158 mg, 93%) as a yellow solid. This complex was dissolved in MeCN (5 mL) and then exposed to sunlight and stirred in air for 30 min. The decomplexation was monitored by TLC ($CHCl_3$/MeOH 9:1). {Note: with the majority of [$Cr(CO)_3$(arene)] complexes, decomplexation via this method takes >2 h}. Filtration through Celite removed the chromium salts and flash chromatography (silica gel, $CHCl_3$/MeOH 9:1) gave **167** as a slightly yellow oil; yield: 91 mg (84%, >98% ee, determined following conversion into the Mosher ester); $[\alpha]_D$ –8.0 (*c* 0.20, $CHCl_3$); ^1H NMR (benzene-d_6, 400 MHz, δ): 6.89 (m, 3H, ArH), 4.10–4.22 (m, 2H), 3.88 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.02 (br s, 1H), 2.75 (br d, 1H, J = 12 Hz), 2.30 (m, 1H), 2.05 (m, 3H), 1.6–1.9 (m, 6H), 1.2 (m, 2H).

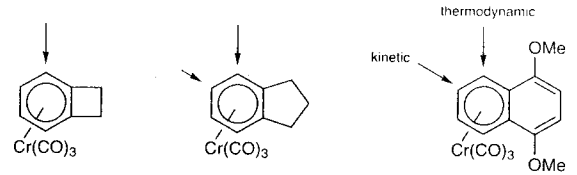
2.4.11.3 Variation 3: Aromatic Substitution via Nucleophile Addition–Oxidation of (Arene)tricarbonylchromium(0) Complexes

(Arene)tricarbonylchromium(0) complexes react with nucleophiles (generated from C—H acids of $pK_a > 22$) by addition to the arene ring *exo* to the tricarbonylchromium moiety. Nucleophiles which can be used in additions to (benzene)tricarbonylchromium(0) in tetrahydrofuran as solvent are[102] $LiCH_2CO_2R^1$, $LiCH_2CN$, $KCH_2COt\text{-}Bu$, $LiCH(CN)(OR^1)$, $LiCH_2SPh$, 2-lithio-1,3-dithianyl, $LiCH{=}CH_2$, PhLi, $LiC{\equiv}CR^1$, $LiCH_2CH{=}CH_2$, and *t*-BuLi. Extensions to other nucleophiles have been reported as well as use of different aromatic systems, and deviations of this pattern have become apparent. Hydride (lithium triethylborohydride) has been shown to add to (benzene)tricarbonylchromium(0) and also to the closely related (benzene)tris(trifluorophosphine)chromium(0) complex.[119,352] Tricarbonylchromium complexes of arenes with imine, oxazoline, or hydrazone substituents react with simple organolithium reagents (e.g., BuLi, MeLi) by addition, rather than by deprotonation as is the case with (benzene)tricarbonylchromium(0) (see Sections 2.4.5.1 and 2.4.5.2). Limitations to the scope of nucleophilic additions to (arene)tricarbonylchromium(0) complexes result from the moderate electrophilicity imparted by the tricarbonylchromium group (comparable to an arene nitro substituent), the activation of the arene hydrogens toward deprotonation, and the potential attack of the nucleophile at a carbonyl ligand.

Nucleophilic additions to substituted arene complexes are often highly regioselective. Resonance donor substituents on the ring direct attack to the *meta* position,[353] while bulky substituents and acceptor substituents direct preferentially *para*.[354] Functional groups that can efficiently coordinate the incoming organolithium reagent direct *ortho*.[121] A number of investigations have described the regioselectivity obtained with various (arene)tricarbonylchromium(0) complexes and different nucleophiles. The results obtained have been related to electronic and steric effects, to the questions of reversibility of nucleophilic attack, to the presence of substituents which coordinate the incoming nucleophile and direct it to a specific position on the arene ring, and to the solvent used.[73,119,121,355,356] In many cases, regioselectivity is complementary to traditional electrophilic substitution. This, and the mild conditions, make it a very useful synthetic method. Scheme 60 indicates preferred sites of nucleophilic addition to a number of complexes.

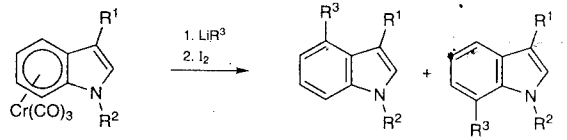
Scheme 60 Regioselectivity in Nucleophilic Addition





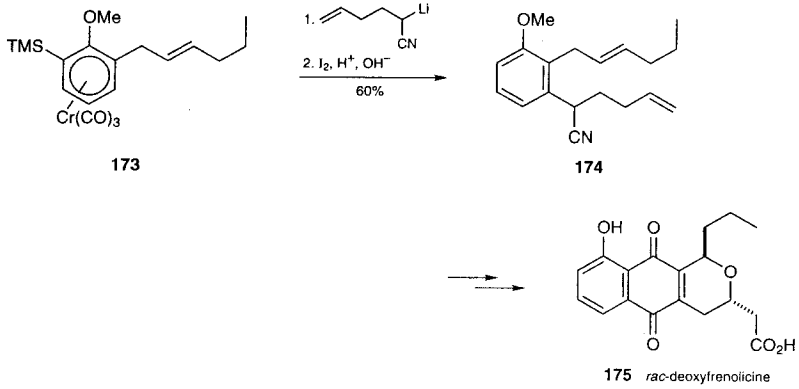
Nucleophilic additions to (arene)tricarbonylchromium(0) complexes afford anionic cyclohexadienyl complexes that can be isolated or, more conveniently for organic transformations, be converted in situ into substituted arenes and chromium(III) salts by oxidation with an excess of iodine, iron(III) salts, or cerium(IV) salts. Examples are shown in Scheme 61. The complexity of regioselectivity in the context of indole alkylation is shown in the examples **170** → **171** + **172**, where steric, thermodynamic, and kinetic factors may dominate, depending on the reaction conditions.[357] The second example depicts the nucleophile addition–oxidation step in a synthesis of *rac*-deoxyfrenolicine (**175**).[358] An intramolecular addition to C4 of the indole complex **176** is the key step in a synthesis of highly diastereoselective synthesis of clavicipitic alcohol (**177**), starting from L-tryptophan.[359]

Scheme 61. Aromatic Substitution via a Nucleophile Addition–Oxidation Sequence with (Arene)tricarbonylchromium(0) Complexes[357–359]



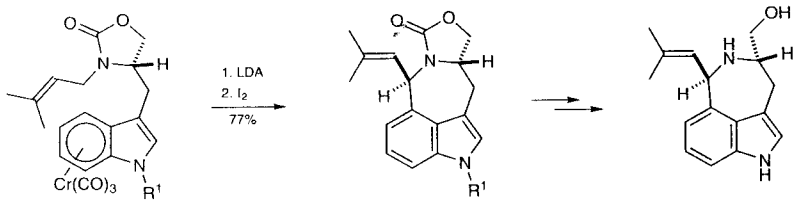
170 **171** **172**

R^1	R^2	R^3	Dominating Factors	Ratio (**171**/**172**)	Yield (%)	Ref.
H	Me	CMe_2CN	thermodynamic	99:1	92	[357]
H	Me	1,3-dithian-2-yl	kinetic	14:86	68	[357]
CH_2TMS	Me	CMe_2CN	steric	17:83	82	[357]
CH_2TMS	TBDMS	CMe_2CN	steric	95:5	78	[357]



173 **174**

175 *rac*-deoxyfrenolicine



176 177 clavicipitic alcohol

2-{2-[(2*E*)-Hex-2-enyl]-3-methoxyphenyl}hex-5-enenitrile (174):[358]

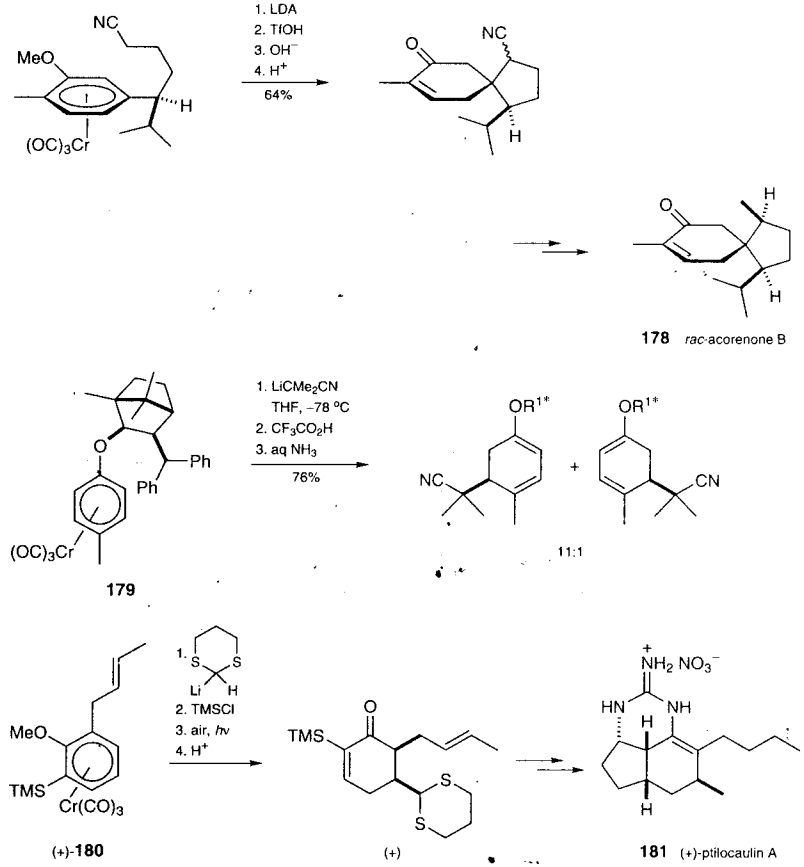
CAUTION: *HMPA is a carcinogen. In many reactions it can be replaced by the safer DMPU.*

To a soln of LDA (0.26 g, 3.3 mmol) in THF (30 mL) in a 100-mL round-bottomed flask under argon at −78 °C was added hex-5-enenitrile[360] (0.314 g, 3.3 mmol). After 1 h, HMPA (10.4 mL, 60 mmol) was added over 2 min, followed by a soln of **173** (1.19 g, 3.0 mmol) in THF (4 mL). After 30 min the mixture was warmed to 0 °C and then cooled to −78 °C. A soln of I_2 (3 g) in THF (10 mL) was then added all at once. The resulting black mixture was warmed to 25 °C for 6 h. The mixture was diluted with Et_2O and washed with sat. aq $NaHSO_3$ (2 ×) and H_2O (1 ×). Rotary evaporation gave an oil to which 1,4-dioxane (50 mL) and 12 M aq HCl (5 mL) were added. The resulting mixture was heated at reflux for 3 h and then cooled to 25 °C and rotary evaporated. The residue was partitioned between Et_2O and H_2O, and the Et_2O layer was washed with H_2O (2 ×) and sat. aq NaCl (1 ×), dried (K_2CO_3), and rotary evaporated to give a dark oil (924 mg). MPLC (hexane/Et_2O 10:1) gave 2-(hex-2-en-1-yl)anisole (78 mg, 14 %), followed by **174**; yield: 511 mg (60%). The ^1H NMR spectrum of **174** showed that it was >95% pure. A portion of **174** was re-chromatographed and distilled (short path, 25–170 °C/0.1 Torr) to give a clear colorless oil for full characterization: ^1H NMR ($CDCl_3$, 90 MHz, δ): 0.85 (t, J = 7.2 Hz, 3H), 1.12–1.56 (m, 2H), 1.71–2.24 (m, 6H), 3.20 (dd, J = 3.8, 14.4 Hz, 1H), 3.48 (dd, J = 4.3, 14.4 Hz, 1H), 3.80 (s, 3H), 4.03 (dd, J = 5.6, 8.6 Hz, 1H), 4.96–6.02 (m, 5H), 6.74–7.36 (m, 3H).

2.4.11.4 Variation 4: Dearomatization Reactions

Dearomatized products result if the anionic tricarbonyl(cyclohexadienyl)chromium(0) complexes are trapped with electrophiles.[361] This was first shown by protonation with a strong acid.[362] The reaction yields mixtures of isomeric cyclohexadienes, whose distribution tends to converge to the most stable diene.[102] Careful choice of temperature and reaction time allows diene regiocontrol and the obtention of single products in the reaction with (anisole)tricarbonylchromium(0). The sequence nucleophile addition–protonation forms the key step in a rapid synthesis of racemic acorenone and acoreneone B (**178**) (Scheme 62).[363] Scheme 62 also depicts two examples of asymmetric methodologies: the first transformation makes use of a chiral auxiliary on the complexed phenol derivative **179** to direct nucleophilic addition,[364] while the second shows a key sequence in an enantioselective total synthesis of (+)-ptilocaulin A (**181**). Chirality here is introduced via the planar chiral anisole complex **117** (see Scheme 40), precursor of the trisubstituted arene complex **180**.[365]

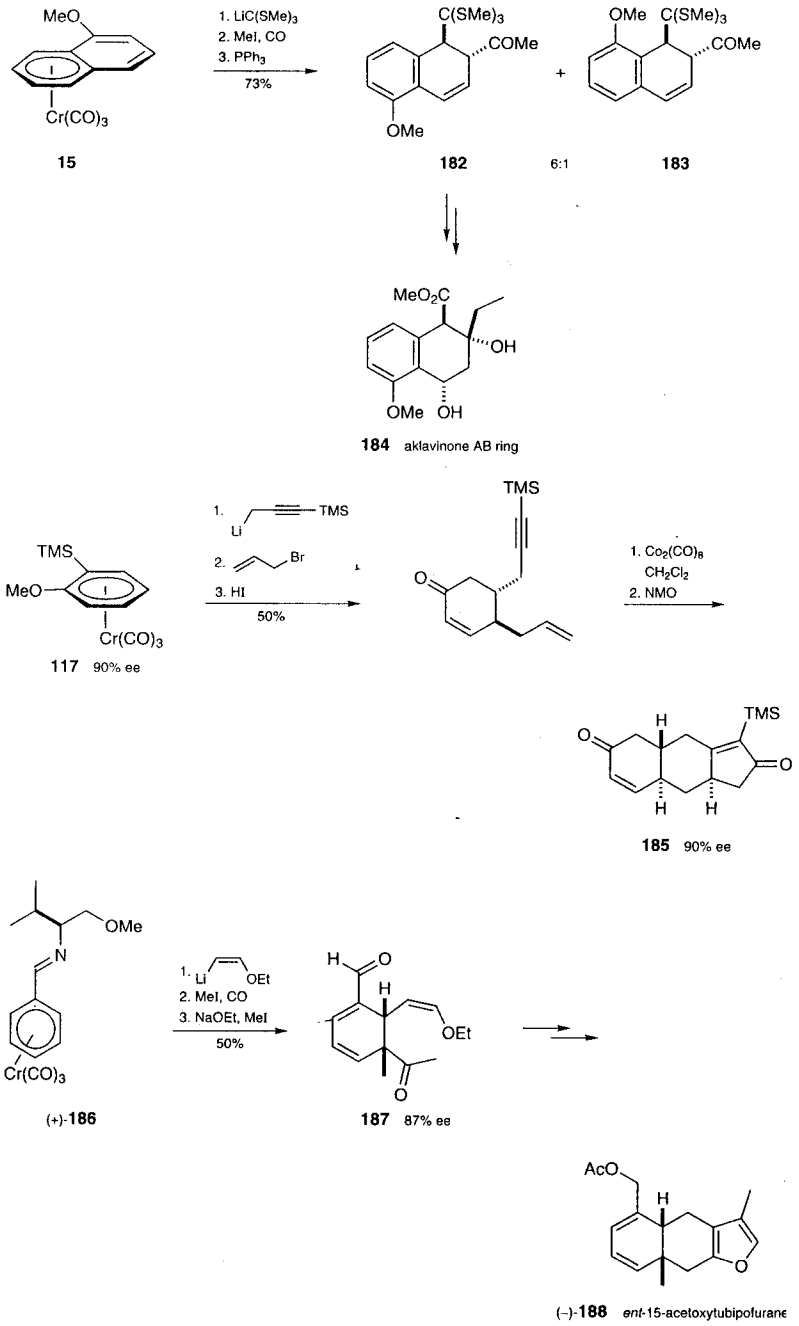
Scheme 62 Regio- and Stereoselective Transformation of Complexed Phenol Derivatives into Substituted Cyclohexenones[363–365]



Trapping of the anionic tricarbonyl(cyclohexadienyl)chromium(0) complexes with reactive carbon electrophiles (primary alkyl iodides, bromides, and tosylates, secondary iodides, allyl and propargyl bromides) affords, after decomplexation, *trans*-substituted cyclohexadienes. Nucleophilic addition (the first step) needs to be irreversible for this reaction sequence to work. The arene substitution pattern and the nature of the electrophile determine whether or not the migration of the C-fragment from the chromium to the cyclohexadienyl ring is preceded by a carbonylation step. Alkyl groups always undergo carbonylation, propargyl groups always migrate directly, and with allyl and benzyl moieties it is the nature of the arene substituents that determine the outcome. Extension of this methodology to the synthesis of enantioenriched products has been successful.[361]

The first example in Scheme 63 shows the key step of a synthesis of the aklavinone AB ring in racemic form (see **184**).[56] This is followed by the transformation of **117** in a highly diastereoselective nucleophilic propargylation–allylation–Pauson–Khand cyclization sequence in which the planar chirality of the starting complex is fully transmitted to the tricyclic product **185**.[242] The last example depicts a key step (**186** → **187**) in an asymmetric synthesis of (–)-15-acetoxytubipofurane (**188**).[366] The efficient transformation of tricarbonylchromium-coordinated arenes into complex chiral molecules represents new and powerful synthetic methodology. Wider applications and further development of this chemistry can be expected.

Scheme 63 Regio- and Stereoselective Transformation of (Arene)tricarbonylchromium(0) Complexes into Alicyclic Products[56,242,366]



***trans*-2-Acetyl-5-methoxy-1-[tris(methylsulfanyl)methyl]-1,2-dihydronaphthalene (182):**[56] To a soln of tris(methylsulfanyl)methane (0.280 mL, 2.04 mmol) in diglyme (10 mL) was added 1.59 M BuLi in hexane (1.28 mL) dropwise at 78 °C. After stirring for 0.5 h,

[$Cr(CO)_3$(5-methoxynaphthalene)] (**15**; 400 mg, 1.36 mmol) was added in one portion as a solid at –78 °C and the temperature was allowed to rise to 10 °C slowly over a period of 3 h. The red soln was stirred another 2 h at 10 °C and then re-cooled to –78 °C. To this dark red soln was added MeI (0.600 mL, 9.6 mmol) and HMPA (2 mL) and then the atmosphere was changed to CO (750 Torr). After stirring for 14 h at 0 °C, Ph_3P (4.0 g, 15.2 mmol) in THF (10 mL) was added and the mixture stirred for 6 h at rt. Et_2O/hexane (1:1, 80 mL) was added and after 1 h at rt the precipitate formed was filtered off. The mother liquor obtained was washed with H_2O (3 × 50 mL), brine (20 mL), dried ($MgSO_4$), and concentrated to give a yellow oil which was purified by column chromatography (30 g silica gel, hexane/Et_2O 10:1) to give a mixture of **182** and **183** (352 mg, 73%) in a 6:1 ratio (by ^1H NMR). Recrystallization (MeOH) yielded pure **182** as colorless prisms; yield: 267 mg (55.4%); mp 100–101 °C; ^1H NMR ($CDCl_3$, 400 MHz δ): 1.98 (s, 9H), 2.19 (s, 3H), 3.81 (s, 3H), 4.04 (s, 1H), 4.21 (d, 1H, J = 6.7 Hz), 6.27 (dd, 1H, J = 9.8, 6.7 Hz), 6.77 (dd, 1H, J = 5.0, 4.0 Hz), 6.98 (d, 1H, J = 9.8 Hz), 7.12 (d, 1H, J = 5.0 Hz), 7.13 (d, 1H, J = 4.0 Hz).

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