Intramolecular Pd-Catalyzed Carbocyclization, Heck Reactions, and Aryl-Radical Cyclizations with Planar Chiral Arene Tricarbonyl Chromium Complexes

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(*o*-butenylhalobenzene)$Cr(CO)_3$ complexes were synthesized by diastereoselectve allylmetal additions to *o*-halo benzaldehyde complexes. The addition of allylZnBr proved particularly convenient and clean. The complexes undergo intramolecular Pd-catalyzed cyclizations (Heck reactions) without decomplexation and/or alkene isomerization. In complexes with a benzylic stereogenic center, the diastereoselectivity of the alkene carbopalladation is governed by the planar chirality of the complex rather than by the benzylic stereogenic center in the side chain. This reaction outcome can be rationalized by the geometry of the arene plane vs that of the Pd coordination plane in the transition step of the alkene carbopalladation step. An alternative cyclization procedure involves the generation of a $Cr(CO)_3$-coordinated arene radical from the bromo and iodo complexes. Intramolecular aryl-radical cyclization affords indan complexes. The transition metal arene π-bond remains intact during this process.

Introduction

Palladium-catalyzed cyclizations of *o*-substituted alkenyl haloarenes or alkenyl phenoltriflates are versatile methods for the preparation of bi- and polycyclic products containing benzylic quaternary carbon centers.[1] The carbopalladation of the alkene by the aryl-Pd fragment results in a new benzylic stereogenic center. Stereochemistry results from discrimination between the prochiral alkene faces by the Pd catalyst. The most powerful method available to achieve high diastereoselectivity in the insertion step is the use of chiral ligands on palladium. Both ligand chirality and mode of reaction (cationic vs neutral pathway) are critical for the outcome of the asymmetric Heck reaction,[2] and elegant applications in synthesis have come forth from several laboratories.[3] Pre-existing chirality in the substrates alkenyl side chain also influences stereochemistry in this sequence. While good diastereoselectivities have been achieved in some reactions, the outcome is often difficult to predict and competing pathways lead to an erosion of observed diastereoselectivities.[4]

Our interest in asymmetric syntheses and applications of planar chiral [(η^6-arene)$Cr(CO)_3$] complexes led us to investigate the possibility of intramolecular Heck reactions and related carbocyclization reactions of these compounds. Enantiomerically pure or enriched planar chiral arene complexes are readily available via efficient resolution procedures,[5] as well as a plethora of elegant diastereoselective and enantioselective routes.[6]

The complexation of a haloarene by a $Cr(CO)_3$ group activates the C_{Ar}−X bond and the chlorobenzene complex undergoes oxidative addition to Pd(0) already at ambient temperature. The literature reports carbonylation[7] and intramolecular cross coupling reactions[8] but intramolecular Heck reactions have not been reported prior to our preliminary communications on this topic.[9,10] We selected the *ortho* butenyl halobenzene complexes **1**−**5** for the study of intramolecular Heck-type reactions. In addition to transition metal-catalyzed cyclizations, radical processes offer complementary methodology,[11] and we briefly looked at the possibility of the generation of an aryl radical on a complexed arene and its use in cyclization processes. This was probed with complexes **2** and **6**.

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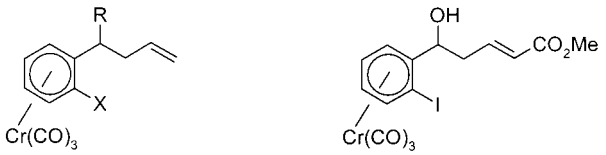
Table 1. The Addition of Allylmetal Halides to Planar Chiral *o*-Halobenzaldehyde Complexes

entry	starting material	allylmetal	addition reaction THF, *T* (°C), t (h)	product	product ratio (*RS*,*RS*)/(*RS*,*SR*)	yield (%)
1	(1*RS*)-**7a**	allylMgBr	−78, 0.5	**2a**	>97:<3	83
2	(1*S*)-(+)-**7a**	allylMgBr	−78, 0.5	(*S*,*S*)-(−)-**2a**	>97:<3	85
3	(1*RS*)-**7a**	allylMgBr	−20, 0.5	**2a**	40:60	80
4	(1*RS*)-**7a**	allylMgBr + 2 equiv $MgBr_2 \cdot OEt_2$	−20, 0.5	**2a**	70:30	80
5	(1*RS*)-**7a**	allylSnBr	50, 2.5	**2a**	>99:<1	78
6	(1*RS*)-**7a**	allylZnBr	25, 2.0	**2a**	>99:<1	90
7	(1*RS*)-**7b**	allylMgBr	−78, 0.5	**2b**	>97:<3	75
8	(1*RS*)-**7b**	allylZnBr	25, 2.0	**2b**	>99:<1	70
9	(1*RS*)-**7c**	allylZnBr	25, 3.0	**2c**	>99:<1	75
10	(1*RS*)-**7c**	allylZnBr	50, 4.0	**6**	>99:<1	55

We note that all these complexes have planar chirality and that **2**−**6** have an additional stereogenic center thus raising the question of the competitive influence of these chiral elements on the stereochemical outcome of the reaction.

Results and Discussion

(a) Synthesis of 1 and Diastereoselective Synthesis of Complexes 2−6. The syntheses of **1a**−**5a**, including their diastereoisomers, all start from a common starting material: the planar chiral *o*-chlorobenzaldehyde complex **7a**.[12] In *ortho*-substituted benzaldehyde complexes the carbonyl group is coplanar with the aromatic ring. It adopts a preferential conformation *anti* to the



1 : R=H
2 : R=OH
3 : R=OMe
4 : R=OSi(t-Bu)Ph_2
5 : R=Me

a : Cl
b : Br
c : I

6

Figure 1.

ortho substituent in order to avoid build-up of $A^{1,3}$-strain.[13] Nucleophilic attack from the side opposite to the $Cr(CO)_3$ group often yields a single diastereoisomer. On the basis of much literature precedent,[5,14] it was therefore expected that the addition of an allylmetal reagent would yield predominantly or exclusively the diastereoisomer (*RS*,*RS*)-**2a**.

As shown in Table 1, this is the case for the addition of allylMgBr at low temperature and for the addition of allylZnBr and allylSnBr reagents.[15] The stereochemical assignment of the major diastereoisomer rests on a comparison of the sign of rotation of the product of the allyl addition to (1*S*)-(+)-**7a** with the literature report of the addition of MeMgBr to the same complex,[16] and on the observation that the (*RS*,*RS*)-diastereoisomer has a higher R_f value on silica gel TLC (0.42 in ether/cyclohexane) than the (*RS*,*SR*)-diastereoisomer (0.08).[17] This tentative assignment was subsequently corroborated by an X-ray structure determination after Pd-catalyzed cyclization (vide infra).

The reaction with allylSnBr[18] is slow and is best carried out by heating to 50 °C (entry 5). As an alternative to

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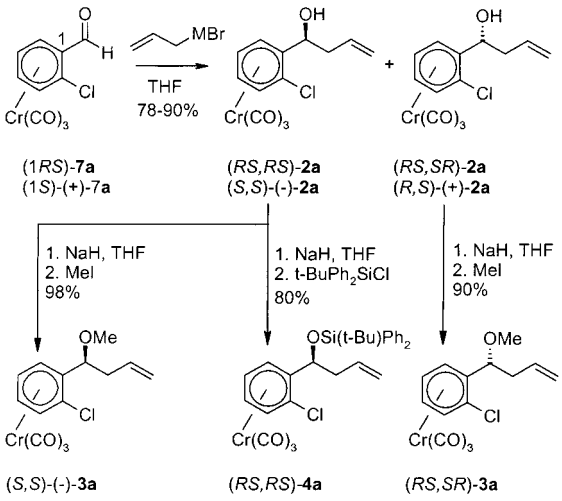
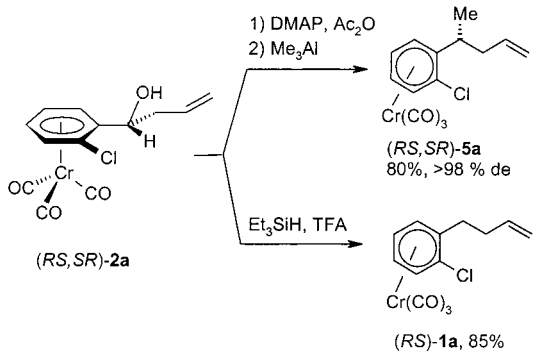
Scheme 1



Scheme 2

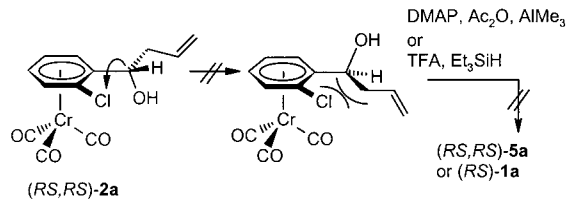


the Grignard reagent addition at low temperature (entry 2), we found that the addition of allylZnBr[19] to **7a** at ambient temperature is a particularly convenient and clean reaction that yielded **2a** as a single diastereoisomer in high yield (entry 6). This procedure was also used for the synthesis of the bromo- and iodo complexes **2b**, **2c**, and **6** (entries 8−10). We note that allylMgBr also adds to **7c** but it also causes the hydrogenolysis of the C_{Ar}−I bond.

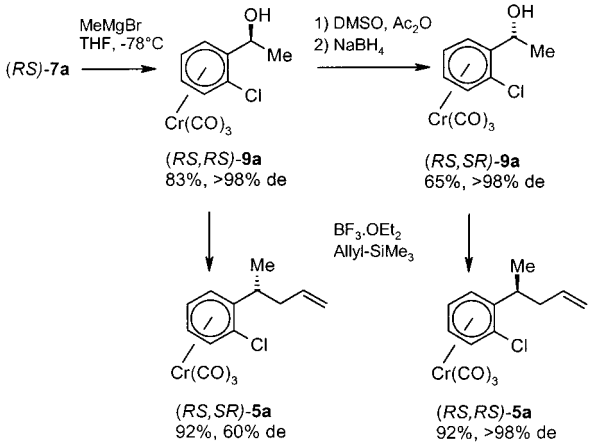
AllylMgBr differs from the other nucleophiles in that it affords a mixture of the readily separable diastereoisomers (*RS,RS*)-**2a** and (*RS,SR*)-**2a** in a 2:3 ratio when the addition is carried out at −20 °C. Complex (*RS,SR*)-**2a** presumably arises from the *syn*-rotamer of **7a** and we attribute the loss of selectivity to the high reactivity of the Grignard reagent. As expected, selectivity shifted back in favor of (*RS,RS*)-**2a** when $MgBr_2$ was added prior to the addition of allylMgBr (entry 4).[14e] The slower reactions of the Zn and Sn reagents and the likelihood of the involvement of Lewis acid activation of the aldehyde in these reactions are advanced as rationale of the high selectivity in these reactions. Lewis acid coordination increases the bulk of the aldehyde substituent and this results in a stronger preference of the *anti*-conformation of the carbonyl group.

Transformation to the methyl and silyl ethers **3a** and **4a** was carried out using standard procedures (see Experimental Section). Ionic hydrogenolysis of the benzylic alcohol function in (*RS,SR*)-**2a** with TFA and Et_3SiH afforded (*RS*)-**1a** in 85% yield, and acetylation of (*RS,SR*)-**2a** followed by reaction with $AlMe_3$ afforded complex (*RS,SR*)-**5a** in 80% overall yield.[20] This reaction occurs with complete retention of configuration, an outcome that is consistent with S_N1-type solvolysis, neighboring group participation of the chromium center in the intermediate, configurationally stable benzylic carbocation, and nucleophilic addition from the side opposite to the metal (Scheme 2).[14a,21]

Scheme 3



Scheme 4



The diastereoisomer (*RS,RS*)-**5a** cannot be obtained by applying the same reaction sequence to the complex (*RS,RS*)-**2a**. The conformer in which the nucleofuge adopts the required *anti* position with respect to the $Cr(CO)_3$ group is unfavorable because of $A^{1,3}$-strain (Scheme 3).[13]

Complex (*RS,RS*)-**5a** was therefore synthesized via the reaction sequence shown in Scheme 4 which involves methyl addition, oxidation/reduction, and allylation of the benzylic cation.[22]

It is interesting to note that this allylation reaction also works with the diastereoisomer (*RS,RS*)-**9a** despite the unfavorable conformation that the complex has to adopt for the cleavage of the C−O bond. This situation is reflected in the erosion of diastereoselectivity of the reaction. Products (*RS,SR*)-**5a** and (*RS,RS*)-**5a** were obtained as a 4:1 mixture of diastereoisomers (Scheme 4).

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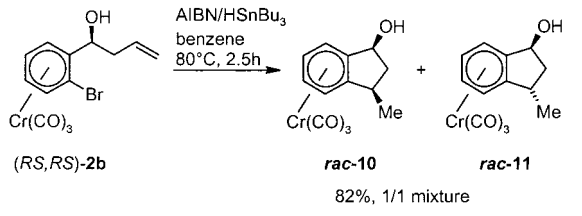
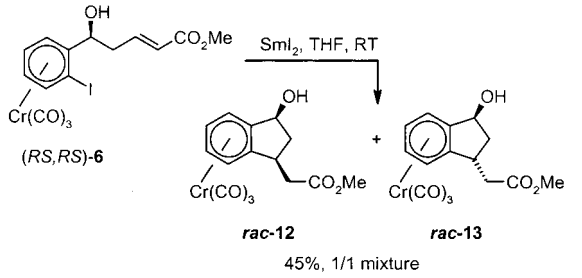
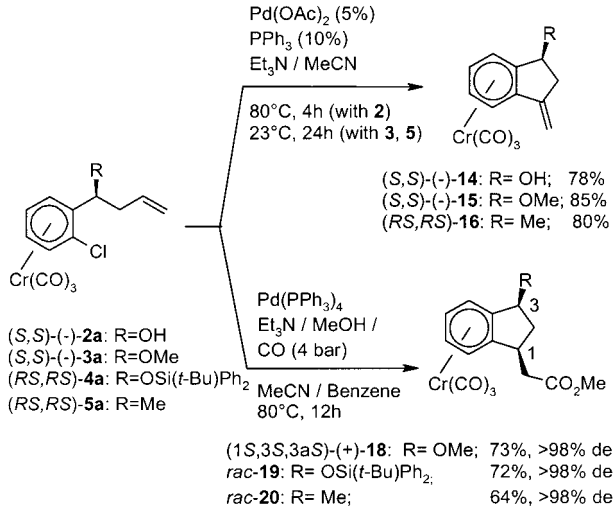
Scheme 5





Scheme 6



(b) Aryl-Radical Generation on (Arene)Cr(CO)$_3$ Complexes and Cyclization. The generation of an aryl radical at the coordinated ring and its use in cyclization reactions is an intriguing possibility that is all the more interesting since $Cr(CO)_3$ bound aryl radicals have not been reported previously and since the study of radical reactions in this class of compounds is still at an early stage.[23] Although we have not carried out a thorough study of this reaction, the results confirm the viability of the approach and it is fitting to include them in this article.

A solution of AIBN, $HSnBu_3$, and (*RS,RS*)-**2a** in benzene ($c = 0.01$ N) at reflux afforded no product other than the starting complex. However, complex (*RS,RS*)-**2b** reacted under these conditions to give the indan complexes **10** and **11** as readily separable diasteromeric mixtures (Scheme 5). The relative stereochemistry was assigned after decomplexation (air, light, CH_3CN) and

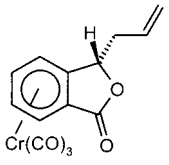


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Figure 2.

comparison of the ^{1}H NMR spectra and the melting points with literature data.[24] Alternatively, samarium(II) iodide can be used for aryl-radical generation.[25] With (*RS,RS*)-**2c**, this afforded complexes **10** and **11** in a low yield only (13%), but with complex (*RS,RS*)-**6**, which contains a more reactive alkene side chain, this process becomes more efficient (Scheme 5). Stereochemical assignment of **12** and **13** rests on the ^{1}H NMR spectral comparison with complex **12** obtained by desilylation (TBAF, THF, rt, 2h) of complex **19**. The preliminary results detailed above show that aryl radicals can be generated from $Cr(CO)_3$-coordinated bromo and iodo arenes and that cyclization reactions can be carried out without cleavage of the arene−$Cr(CO)_3$ bond albeit that diastereoselection in this process is not induced by the planar chirality of the starting material or by the benzylic stereogenic center. This situation is different in the Pd-catalyzed reactions described below.

(c) Intramolecular Heck Reactions and Related Carbocyclizations with Planar Chiral Arene−Cr(CO)$_3$ Complexes. Complex (*S,S*)-(−)-**2a** cleanly underwent an intramolecular Heck reaction in refluxing acetonitrile yielding the methylene indan complex (*S,S*)-(−)-**14** as a single product (Scheme 6). With complexes (*S,S*)-(−)-**3a** and (*RS,RS*)-**5a** the reaction temperature could be lowered to 23 °C. We take this as an indication that the OH group competes for the same Pd-coordination site as the alkene. Despite the increased lability of complexes of arenes with conjugated alkene substituents, the $Cr(CO)_3$ coordination remained intact and no isomerization to an indene complex took place under the reaction conditions.[26]

While the transformations yielding **14**−**16** show that Pd-catalyzed intramolecular cyclizations can be efficiently realized, the β-elimination that terminates the reaction sequence destroys the stereogenic center created in the carbopalladation step. To probe the stereochemical influence of the chiral elements present in **2**−**5** (the planar chirality of the complexed arene and the stereogenic benzylic center), the termination step was modified and cyclization was carried out in the presence of CO and methanol (Scheme 6). Initial reactions with the hydroxy complex *rac*-**2a** afforded the γ-lactone *rac*-**17** (Figure 2) in 70% yield rather than the carbocyclic product *rac*-**12** (or *rac*-**13**) showing that carbonylation followed by lactonization is faster than alkene insertion in this case. The

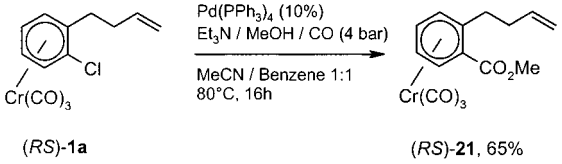
(23) For radical addition reactions to arene−$Cr(CO)_3$ complexes see: (a) Schmalz, H. G.; Siegel, S.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2383. (b) Schmalz, H. G.; Siegel, S.; Schwarz, A. *Tetrahedron Lett.* **1996**, *37*, 2947. For reactions with arene−$Cr(CO)_3$ complexed benzylic radical see: (c) Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem.* **1996**, *61*, 6088. (d) Taniguchi, N.; Uemura, M. *Tetrahedron Lett.* **1997**, *38*, 7199. (e) Merlic, C.; Walsh, J. C. *Tetrahedron Lett.* **1998**, *39*, 2083. (f) Taniguchi, N.; Hata, T.; Uemura, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1232.

(24) (a) Jaouen, G.; Dabard, R. *Tetrahedon Lett.* **1971**, *15*, 1015. (b) Miura, M.; Yoshida, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1982**, 79.

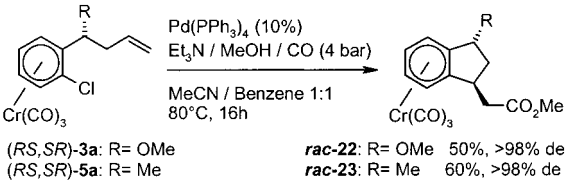
(25) (a) Curran, D. P.; Fevig, T. L.; Totleben, M. J. *Synlett* **1990**, 773. (b) Inagana, J.; Ujikawa, O.; Yamaguchi, M. *Tetrahedron Lett.* **1991**, *32*, 1737.

(26) Longer reaction times and/or higher temperatures led to decomplexed, partially isomerized products. We note that the use of Ag salts in these reactions is incompatible with the oxidation sensitive $Cr(CO)_3$ group.

Scheme 7



Scheme 8



complexes (*S*,*S*)-(−)-**3a**, (*RS*,*RS*)-**4a**, and (*RS*,*RS*)-**5a** on the other hand reacted as expected to yield products (+)-**18**, *rac*-**19**, and *rac*-**20**, respectively, as single diastereoisomers. The anti relationship between the ester function and the $Cr(CO)_3$ fragment was confirmed by a crystal structure analysis of complex *rac*-**19**. A list of selected bond lengths and angles is given in the Supporting Information.

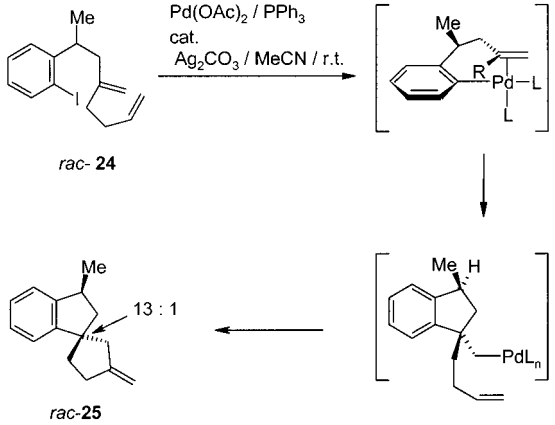
The six carbons atoms of the arene ring lie in a mean plane (maximum deviation of 0.016 Å) with the Cr atom located at 1.686(1) Å above the plane. The *exo* CH_2CO_2-Me group and of the *exo* silyl substituent result in an envelope conformation of the five-membered ring with the methylene C-atom out of plane (0.46(1) Å) toward the chromium tripod. The $Cr(CO)_3$ fragment adopts a staggered conformation with respect to the arene ring, a situation frequently observed in *ortho* disubstituted arene−$Cr(CO)_3$ complexes.[27]

Under similar conditions, complex (*RS*)-**1a** afforded the ester (*RS*)-**21** (Scheme 7). As in the reaction of the hydroxy complex **2a**, CO insertion is faster than alkene insertion in this case.

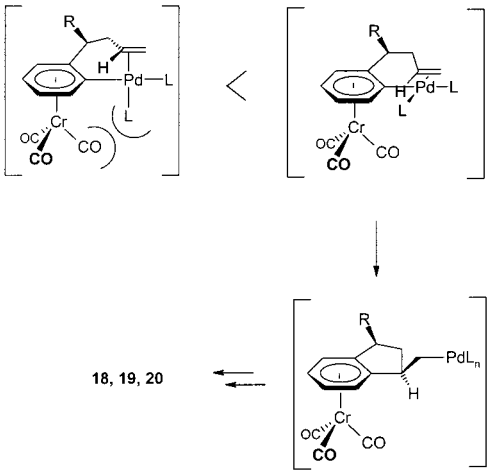
Scheme 8 depicts the outcome of the reaction wih the (*RS*,*SR*)-diastereoisomers of **3a** and **5a**. The *anti*-relationship between the $Cr(CO)_3$ fragment and the CH_2CO_2-Me group in both **22** and **23** shows that the diastereofacial selectivity of the alkene carbopalladation is controlled by the planar chirality of the complex rather than by the benzylic chiral center. The planar chirality thus overrules the influence of the benzylic stereogenic center manifest in *Overmans* polyene cyclization reaction of *rac*-**24** shown in Scheme 9.[4] While the reaction conditions differ in a number of elements from those reported here, notably in their use of a Ag salt, a comparison of the probable reasons for this difference is of interest.

The transition state geometry of the Heck reaction favors an eclipsed arrangement of the alkene to the Pd−C(Ar) bond.[28] For the Pd-catalyzed polycyclyzation of *rac*-**24**, a geometry for the insertion step was proposed in which the benzylic substituent adopts an equatorial position and the alkene coordinates to the Pd with its Re face to lead to the observed major diastereoisomer *rac*-**25**. (Scheme 9).

Scheme 9



Scheme 10



When applied to the $Cr(CO)_3$ complexes **3**−**5**, this arrangement would lead to severe steric congestion between the $Cr(CO)_3$ group and one of the phosphine ligands. However, a coordination to the diastereotopic alkene face would result in the transition state as shown in Scheme 10 and provide a rationale for the observed diastereoselectivity.

In conclusion, we have shown that easily prepared planar chiral arene chromium complexes can be used successfully in either palladium-catalyzed carbocyclization, Heck reactions, or aryl-radical cyclization to afford indan complexes. In the case of the intramolecular Pd-catalyzed alkene carbopalladation with *o*-substituted chlorobenzene complexes, we have demonstrated that the stereoselectivity of the reaction is completely governed by the planar chirality of the complex.

Experimental Section

General. Reactions and manipulations involving organometallic compounds were carried out under an atmosphere of purified nitrogen using an inert gas/vacuum double manifold and standard Schlenk techniques. Flash column chromatography was carried out in air (silica gel: Merck 60). All NMR spectra (^1H, 200 or 400 MHz; ^{13}C, 50.3 or 100.5 MHz) were recorded at room temperature on a Varian XL-200 or Bruker 400 MHz spectrometer as indicated. Chemical shifts (δ) are reported relative to TMS as the internal standard. Mass spectra were obtained on a Varian CH4 or SM1 spectrometer, relative intensities are given in parentheses. High-resolution mass spectra were measured on a VG analytical 7070E instrument (data system 11250, resolution 7000). IR spectra

(27) (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (b) Kündig, E. P.; Grivet, C.; Wenger, E.; Bernardinelli, G.; Williams, A. F. *Helv. Chim. Acta* **1991**, *74*, 2009.

(28) (a) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. (b) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505. (c) Overman, L. E.; Poon, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 518.

were recorded in NaCl cells on a Perkin-Elmer 1650 FT-IR spectrometer. Melting points were determined on a Büchi 510 apparatus and are not corrected. THF and diethyl ether were dried and distilled from sodium/benzophenone ketyl under N_2 before use. Dichloromethane and hexane were freshly distilled from CaH_2 under N_2. All chemicals were purchased from Aldrich or Fluka.

(η^6-2-Bromobenzaldehyde)Cr(CO)$_3$ ((*RS*)-7b). To a stirred solution of tricarbonyl(η^6-2-phenyl-1,3-dioxolane)chromium[29] (2.002 g, 7.00 mmol) in THF (50 mL) was added *n*BuLi (4.81 mL, 1.6 N in hexane, 7.70 mmol) at −78 °C. After the mixture was stirred for 2 h, 1,2-dibromotetrachloroethane (2.735 g, 8.400 mmol) was added and stirring continued for 30 min. The reaction mixture was quenched with aqueous NH_4Cl and filtered through SiO_2 (Et_2O). Hydrolysis of the acetal function was carried out directly by addition of HCl (11 mL, 2 N, 22 mmol) overnight. Extraction (Et_2O/H_2O) and column chromatography (SiO_2, Et_2O/Hx 1−2) gave the complex (*RS*)-**7b** as a red solid (1.680 g, 75%). Mp: 62−63 °C (recrd, Et_2O/Hx). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.90 (s, 1H), 6.19 (d, 1H, J = 6.4 Hz), 5.70 (t, 1H, J = 6.0 Hz), 5.45 (d, 1H, J = 6.4 Hz), 5.19 (t, 1H, J = 6.0 Hz). ^{13}C NMR (C_6D_6, 100 MHz): δ 229.4, 186.9, 93.9, 92.2, 92.1, 89.0, 86.6, 65.2. IR (Hexane): 2002, 1942, 1695. MS (*m*/*z*): 322(16), 320(17), 266(2), 264(2), 157(73), 149(26), 105(19), 77(13), 52(100); HRMS Calcd. for $C_{10}H_5{}^{79}BrCrO_4$: 319.8776. Found: 319.8787. Calcd for $C_{10}H_5{}^{81}BrCrO_4$: 321.8755. Found: 321.8733.

(η^6-2-Iodobenzaldehyde)Cr(CO)$_3$ ((*RS*)-7c). To a stirred solution of tricarbonyl(η^6-2-phenyl-1,3-dioxolane)chromium (5.000 g, 17.50 mmol) in THF (70 mL) was added *n*BuLi (13.00 mL, 1.6 N in hexane, 20.80 mmol) at −78 °C. After the mixture was stirred for 2 h, iodine (5.200 g, 20.50 mmol) was added and stirring continued for 30 min. The reaction mixture was quenched with aqueous NH_4Cl followed by an extraction (Et_2O/H_2O). Hydrolysis of the acetal function was carried out by treatment with acidic aqueous (HCl, 30 mL, 3 N) THF (50 mL) overnight. Extraction (Et_2O/H_2O) and column chromatography (SiO_2, Et_2O/Hx 1−1) gave the complex (*RS*)-**7c** as a red solid (3.807 g, 60%). Mp: 102−104 °C (Et_2O/Hx). ^{1}H NMR (C_6D_6, 200 MHz): δ 9.36 (s, 1H), 5.53 (dd, 1H, J = 6.5, 1.3 Hz), 4.47 (dd, 1H, J = 6.5, 1.0 Hz), 4.19 (td, 1H, J = 6.1, 1.3 Hz), 3.89 (t, 1H, J = 6.0 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 230.2, 190.9, 98.4, 95.1, 93.5, 92.9, 87.8, 65.9. IR (Hexane): 2000, 1941, 1697. MS (*m*/*z*): 368(17), 284(44), 207(32), 181(18), 157(94), 105(12), 52(100). HRMS Calcd for $C_{10}H_5CrIO_4$: 367.8637. Found: 367.8655.

General Procedure for the Addition of AllylMgBr to (*o*-Halobenzaldehyde)Cr(CO)$_3$ (7a−b). A solution of the allyl-Grignard reagent (2.2 equiv, in Et_2O) was added dropwise to a solution of the *o*-substituted benzaldehyde complex in THF. After 30 min, the yellow reaction mixture was quenched with aqueous NH_4Cl, extracted with Et_2O, and dried over $MgSO_4$. The residue was then purified by column chromatography (SiO_2, Et_2O/Hx).

(1-(η^6-2-Chloro-phenyl)-but-3-en-1-ol)Cr(CO)$_3$ (*RS,RS*) and ((*S,S*)-(−)-2a). The general procedure described above with the allyl-Grignard reagent was carried out at −78 °C with the *o*-chloro-benzaldehyde complex (*RS*)-**7a** (1.125 g, 4.069 mmol) to afford (*RS,RS*)-**2a** as a yellow oil (1.076 g, 83%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.78−5.55 (m, 1H), 5.31 (d, 1H, J = 6.1 Hz), 5.02−4.82 (m, 2H), 4.55 (d, 1H, J = 6.3 Hz), 4.48−4.41 (m, 1H), 4.3 (t, J = 6.3 Hz, 1H), 4.08 (t, 1H, J = 6.1 Hz), 2.32−2.18 (m, 1H), 2.12−1.95 (m, 1H), 1.70 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 231.8, 133.1, 119.2, 111.8, 111.1, 92.7, 91.8, 90.0, 89.1, 68.2, 42.2. IR (CH_2Cl_2): 1975, 1895. MS (*m*/*z*): 318(18), 262(12), 180(84), 130(100), 129(99), 115(37), 52(99). HRMS Calcd for $C_{13}H_{11}ClCrO_4$: 317.9751. Found: 317.9778. This procedure was applied to (*S*)-(+)-**7a** (0.600 g, 2.170 mmol scale) to afford (*S,S*)-(−)-**2a** (0.590 g, 85%). $[\alpha]_D^{20} = -5.9$ (c = 0.92, $CHCl_3$).

(1-(η^6-2-Chloro-phenyl)-but-3-en-1-ol)Cr(CO)$_3$ ((*RS,SR*)-2a). The general procedure using the allyl-Grignard reagent was carried out at −20 °C with (*RS*)-**7a** (0.276 g, 1.00 mmol) to afford a yellow oil shown by ^{1}H NMR to consist of a 2:3 mixture of (*RS,RS*)-**2a** and (*RS,SR*)-**2a**. The diastereoisomers were readily separated by column chromatography (SiO_2, Et_2O/Hx 1−2). Data for (*RS,SR*)-**2a**. ^{1}H NMR (C_6D_6, 200 MHz): δ 5.80−5.60 (m, 1H), 5.23 (dd, 1H, J = 6.5, 1.2 Hz), 5.12−4.96 (m, 2H), 4.54 (dd, 1H, J = 6.5, 1.2 Hz), 4.48−4.36 (m, 2H), 3.99 (td, 1H, J = 6.3, 1.1 Hz), 2.70−2.52 (m, 1H), 2.41−2.25 (m, 1H), 1.78 (d, 1H, J = 4.2 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.3, 134.4, 118.9, 114.1, 110.5, 94.2, 93.5, 90.0, 86.6, 69.1, 42.8. IR (CH_2Cl_2): 1975, 1902. MS (*m*/*z*): 318(7), 180(33), 157(5), 129(61), 115(23), 77(20), 52(100). HRMS Calcd for $C_{13}H_{11}ClCrO_4$: 317.9751. Found: 317.9762.

(1-(η^6-2-Bromo-phenyl)-but-3-en-1-ol)Cr(CO)$_3$ ((*RS,RS*)-2b). The general procedure using the allyl-Grignard reagent was carried out at −78 °C with (*RS*)-**7b** (0.900 g, 2.803 mmol) to afford the complex (*RS,RS*)-**2b** as a yellow oil (0.762 g, 75%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.83−5.55 (m, 1H), 5.28 (d, 1H, J = 6.2 Hz), 5.05−4.82 (m, 2H), 4.65 (d, 1H, J = 6.3 Hz), 4.41−4.32 (m, 1H), 4.20 (t, 1H, J = 6.1 Hz), 4.10 (t, 1H, J = 6.1 Hz), 2.31−2.18 (m, 1H), 2.11−1.95 (m, 1H), 1.70 (bs, 1H). ^{13}C NMR (C_6D_6, 50 MHz): δ 233.1, 133.8, 126.1, 118.2, 113.1, 95.1, 93.1, 90.5, 89.1, 70.5, 42.1. IR (Hexane): 1985, 1922. MS (*m*/*z*): 364(11), 362(11), 308(2), 306(2), 262(3), 260(3), 180(79), 157(12), 130(75), 128(75), 77(18), 52(100). HRMS Calcd for $C_{13}H_{11}{}^{79}BrCrO_4$: 361.9245. Found: 361.9278. Calcd for $C_{13}H_{11}{}^{81}BrCrO_4$: 363.9225. Found: 363.9256.

General Procedure for the Addition of AllylZnBr to (*o*-Halobenzaldehyde)Cr(CO)$_3$ (7a−c). Allylbromide (1.50 mmol) in THF (1.5 mL) was added dropwise to a stirred solution of zinc dust (1.50 mmol) in THF (3 mL) at room temperature and the mixture stirred for 30 min. The benzaldehyde complex (1.00 mmol) in THF (1 mL) was then added and stirring was continued until completion of the reaction (followed by TLC). The reaction mixture was quenched with water and extracted with portions of Et_2O. The combined organic phases were washed with water and brine and then dried over $MgSO_4$. Concentration, followed by column chromatography (SiO_2, Et_2O/Hx) afforded the product.

(1-(η^6-2-Chloro-phenyl)-but-3-en-1-ol)Cr(CO)$_3$ ((*RS,RS*)-2a). The general procedure described above was used with (*RS*)-**7a** (0.276 g, 1.00 mmol) to afford (*RS,RS*)-**2a** (0.286 g, 90%).

(1-(η^6-2-Bromo-phenyl)-but-3-en-1-ol)Cr(CO)$_3$ ((*RS,RS*)-2b). The general procedure described above was used with (*RS*)-**7b** (0.170 g, 0.530 mmol) to afford the complex (*RS,RS*)-**2b** (0.138 g, 70%).

(1-(η^6-2-Iodo-phenyl)-but-3-en-1-ol)Cr(CO)$_3$ ((*RS,RS*)-2c). The general procedure described above was used with (*RS*)-**7c** (0.650 g, 1.770 mmol) to afford the complex (*RS,RS*)-**2c** as a yellow oil (0.510 g, 75%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.82−5.55 (m, 1H), 5.27 (d, 1H, J = 6.4 Hz), 5.05−4.90 (m, 2H), 4.86 (d, 1H, J = 6.4 Hz), 4.30−4.20 (m, 2H), 4.14 (dt, 1H, J = 6.2, 1.0 Hz), 2.35−2.22 (m, 1H), 2.10−1.95 (m, 1H), 1.70 (d, 1H, J = 4.2 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.9, 133.8, 118.5, 115.6, 100.9, 93.3, 90.6, 90.0, 74.5, 65.6, 42.7. IR (Hexane): 1984, 1925. MS (*m*/*z*): 410(22), 354(4), 308(16), 256(5), 199(20), 180(90), 129(65), 115(24), 52(100). HRMS Calcd for $C_{13}H_{11}CrIO_4$: 409.9107. Found: 409.9121.

(1-(η^6-2-Iodo-phenyl)-4-*trans*-methylester-but-3-en-ol)-Cr(CO)$_3$ ((*RS,RS*)-6). Methyl-*trans*-4-bromo-2-butenoate (0.330 mL, 2.816 mmol) in THF (3.0 mL) was added dropwise to a stirred solution of zinc dust (0.160 g, 2.470 mmol) in THF (2 mL) at 50 °C. After 1h, a solution of (*RS*)-**7c** (0.650 g, 1.760 mmol) in THF (1.0 mL) was added and stirring was continued for 4h to afford after extraction (Et_2O/H_2O) and column chromatography (SiO_2, Et_2O/Hx 1−1) the complex (*RS,RS*)-**6** as a yellow oil (0.450 g, 55%). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.20−7.05 (m, 1H), 5.90 (d, 1H, J = 15.7 Hz), 5.26 (dd, 1H, J = 6.4, 0.8 Hz), 4.86 (dd, 1H, J = 6.6, 1.0 Hz), 4.32−4.21 (m, 2H), 4.16 (dt, 1H, J = 6.2, 1.2 Hz), 3.45 (s, 3H), 2.45 (bs, 1H), 2.32−2.18 (m, 1H), 2.10−1.95 (m, 1H). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.7, 166.6, 144.3, 124.3, 114.9, 100.6, 93.6, 90.5, 89.9, 74.1, 65.9, 51.4, 40.9. IR (Hexane): 1985, 1927, 1750. MS (*m*/*z*): 468(8), 412(4), 369(6), 328(5), 284(14), 211(8),

(29) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans. 1* **1989**, 192.

157(100), 129(64), 52(99). HRMS Calcd for $C_{15}H_{13}CrIO_6$: 467.9162. Found: 467.9199.

(1-Chloro-2-(1-methoxybut-3-enyl)-η^6-benzene)Cr(CO)$_3$ ((*RS,SR*)-3a). To a suspension of NaH (16.5 mg, 0.70 mmol) in THF (10 mL) was added slowly the complex (*RS,SR*)-**2a** (0.200 g, 0.620 mmol) in THF (4 mL) at −20 °C followed, after 30 min at 0 °C, by MeI (0.178 g, 1.250 mmol). The mixture was stirred for 1h, and then the reaction mixture was hydrolyzed with water and extracted with Et_2O. Flash chromatography (SiO_2, Et_2O/Hx 1−1) afforded the complex (*RS,SR*)-**3a** as a yellow solid (0.188 g, 90%). Mp: 63−64 °C (recrd, Et_2O/Hx). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.96 (ddt, 1H, J = 17.2, 10.3, 6.8 Hz), 5.25 (dd, 1H, J = 6.5, 1.1 Hz), 5.23−5.03 (m, 2H), 4.48 (dd, 1H, J = 6.4, 1.3 Hz), 4.40 (td, 1H, J = 6.1, 1.2 Hz), 4.18 (t, 1H, J = 6.8 Hz), 3.88 (td, 1H, J = 6.3, 1.4 Hz), 2.89 (s, 3H), 2.70−2.60 (m, 2H). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.2, 134.8, 117.7, 115.1, 109.0, 94.6, 94.2, 88.8, 85.7, 78.7, 57.1, 42.9. IR (CH_2Cl_2): 1976, 1904. MS (*m*/*z*): 332(7), 216(6), 180(68), 131(40), 129(70), 89(13), 87(10), 52(100). HRMS Calcd for $C_{14}H_{13}ClCrO_4$: 331.9907. Found: 331.9868.

(1-Chloro-2-(1-methoxybut-3-enyl)-η^6-benzene)Cr(CO)$_3$ ((*S,S*)-(−)-3a). To a suspension of NaH (14.5 mg, 0.60 mmol) in THF (10 mL) was added slowly the complex (S,S)-(−)-**2a** (0.175 g, 0.550 mmol) in THF (4 mL) at −20 °C, followed, after 30 min at 0 °C, by MeI (0.234 g, 1.650 mmol). Stirring was continued for 1h, and the reaction mixture was hydrolyzed with water and extracted with Et_2O. Flash chromatography (SiO_2, Et_2O/Hx 1−1) afforded the complex (*S,S*)-(−)-**3a** as a yellow solid (179 mg, 98%). Mp: 54−55 °C (recrd, Et_2O/Hx). $[\alpha]_D^{20}$ = −77 (c = 0.96, $CHCl_3$). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.82−5.60 (m, 1H), 5.29 (dd, 1H, J = 6.4; 1.4 Hz), 5.02−4.85 (m, 2H), 4.54 (d, 1H, J = 1.1 Hz), 4.31 (td, 1H, J = 6.4, 1.4 Hz), 4.18 (dd, 1H, J = 6.5, 4.1 Hz), 4.02 (td, 1H, J = 6.3, 1.0 Hz), 3.30 (s, 3H), 2.40−2.28 (m, 1H), 2.22−2.05 (m, 1H). ^{13}C NMR (C_6D_6, 50 MHz): δ 231.8, 133.1, 119.2, 111.8, 111.1, 92.7, 91.8, 90.1, 90.0, 68.8, 58.6, 42.2. IR (CH_2Cl_2): 1975, 1901. MS (*m*/*z*): 332(9), 276(11), 216(8), 207(6), 180(71), 130(47), 129(64), 89(18), 52(100). HRMS Calcd for $C_{14}H_{13}ClCrO_4$: 331.9907. Found: 331.9902.

(Diphenyl-terbutyl-(1-(η^6-2-chloro-phenyl)-but-3-enyl-oxy))-silane)Cr(CO)$_3$ ((*RS,RS*)-4a). To a suspension of KH (37.6 mg, 0.940 mmol) in THF (10 mL) was slowly added the complex (*RS,RS*)-**2a** (0.250 g, 0.780 mmol) in THF (4 mL) at −20 °C followed, after 30 min at 0 °C, by Si*t*BuPh$_2$Cl (0.280 g, 1.020 mmol). After 1 h at room temperature, the reaction mixture was hydrolyzed with water and extracted with Et_2O. Flash chromatography (SiO_2, Et_2O/Hx 1−1) afforded the complex (*RS,RS*)-**4a** as a yellow solid (0.349 g, 80%). Mp: 98−99 °C (Hx). ^{1}H NMR (C_6D_6, 200 MHz): δ 8.02−7.95 (m, 2H), 7.90−7.80 (m, 2H), 7.45−7.35 (m, 2H), 7.30−7.20 (m, 4H,), 5.71 (dd, 1H, J = 6.4, 1.1 Hz), 5.59 (ddt, 1H, J = 17.3, 10.5, 7.5 Hz), 5.30 (dd, 1H, J = 5.1, 3.5 Hz), 4.85−4.75 (m, 1H), 4.62−4.53 (m, 1H), 4.49 (dd, 1H, J = 6.3, 1.0 Hz), 4.41 (td, 1H, J = 6.2, 1.2 Hz), 4.10 (td, 1H, J = 6.2, 1.2 Hz), 2.35−2.20 (m, 2H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 231.9, 136.1, 134.0, 132.2, 131.7, 130.0, 127.7, 119.0, 111.3, 111.0, 93.7, 91.6, 89.9, 86.7, 70.6, 41.4, 27.2, 19.4. IR (CH_2Cl_2): 1975, 1901. MS (*m*/*z*): 556(9), 500(1), 472(94), 363(35), 343(29), 285(69), 249(59), 135(49), 52(100). HRMS Calcd for $C_{29}H_{29}ClCrO_4Si$: 556.0929. Found: 556.0898.

(2-(η^6-2-Chloro-phenyl)-pent-4-ene)Cr(CO)$_3$ ((*RS,SR*)-5a). Acetic anhydride (0.380 mL, 3.80 mmol) and DMAP (0.450 g, 3.80 mmol) were added to a CH_2Cl_2 (40 mL) solution of complex (*RS,SR*)-**2a** (1.100 g, 3.50 mmol), and stirring continued for 2 h. Successive extractions with NH_4Cl, $NaHCO_3$, and brine afforded the acetate complex which was used in the next step without further purification: (1-(η^6-2-chloro-phenyl)-but-3-en-1-OAc)Cr(CO)$_3$. ^{1}H NMR (C_6D_6, 200 MHz): δ 5.94 (dd, 1H, J = 8.9, 6.3 Hz), 5.78−5.62 (m, 1H), 5.15−4.95 (m, 3H), 4.45 (dd, 1H, J = 6.5, 1.1 Hz), 4.39 (dt, 1H, J = 6.4, 1.1 Hz, ar-*H*), 3.87 (dt, 1H, J = 6.4, 1.0 Hz), 2.72−2.58 (m, 2H), 1.63 (s, 3H). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.6, 168.9, 133.3, 118.6, 114.7, 107.1, 94.4, 93.7, 89.5, 85.6, 70.8, 40.7, 20.5. IR (CH_2Cl_2): 1978, 1907, 1740. MS (*m*/*z*): 360(2), 304(12), 239(44), 180(14), 130(100), 111(34), 52(72). HRMS Calcd for $C_{15}H_{13}ClCrO_5$: 359.9856. Found: 359.9816.

The crude product was dissolved in CH_2Cl_2 (35 mL) and cooled at −78 °C. An $AlMe_3$ solution in hexane (19%, 7.23 mL, 12.25 mmol) was added dropwise and stirring continued while warming from −78 °C to 0 °C over a period of 3h. The reaction mixture was quenched with NH_4Cl. Extraction (Et_2O/H_2O) and column chromatography (SiO_2, Et_2O/Hx 1−1) afforded the complex (*RS,SR*)-**5a** as a yellow solid (0.880 g, 80%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.75−5.55 (m, 1H), 5.12−4.98 (m, 2H), 4.66 (dd, 1H, J = 6.4, 1.1 Hz), 4.55 (dd, 1H, J = 6.2, 1.3 Hz), 4.34 (dt, 1H, J = 6.3, 1.3 Hz), 4.06 (dt, 1H, J = 6.3, 1.1 Hz), 2.90−2.80 (m, 1H), 2.55−2.40 (m, 1H), 1.95−1.80 (m, 1H), 0.92 (d, 3H, J = 6.8 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.6, 136.1, 117.4, 115.5, 113.1, 92.3, 91.6, 90.7, 88.8, 40.0, 34.9, 21.3. IR (CH_2Cl_2): 1972, 1898. MS (*m*/*z*): 316(24), 276(4), 232(23), 196(46), 145(87), 87(15), 52(100). HRMS Calcd for $C_{14}H_{13}ClCrO_3$: 315.9958. Found: 315.9948.

(1-(η^6-2-Chloro-phenyl)-but-3-ene)Cr(CO)$_3$ ((*RS*)-1a). Triethylsilane (0.960 mL, 6.20 mmol) and TFA (0.480 mL, 6.20 mmol) were added to a CH_2Cl_2 (8 mL) solution of complex (*RS,SR*)-**2a** (0.400 g, 1.240 mmol) and the mixture was stirred (room temperature, 1h). The solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, Et_2O/Hx 1−2) to afford the complex (*RS*)-**1a** as a yellow oil (0.320 g, 85%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.65−5.45 (m, 1H), 4.95−4.80 (m, 2H), 4.71 (dd, 1H, J = 6.5, 1.1 Hz), 4.40 (dd, 1H, J = 6.2, 1.4 Hz), 4.24 (dt, 1H, J = 6.3, 1.4 Hz), 4.08 (dt, 1H, J = 6.2, 1.0 Hz), 2.68−2.50 (m, 1H), 2.10−1.90 (m, 3H). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.5, 136.5, 116.2, 112.1, 108.9, 93.4, 92.6, 91.4, 89.6, 34.4, 32.6. IR (CH_2Cl_2): 1973, 1899. MS (*m*/*z*): 302(31), 246(3), 218(27), 182(53), 180(64), 131(92), 91(30), 52(100). HRMS Calcd for $C_{13}H_{11}ClCrO_3$: 301.9801. Found: 301.9815.

(1-(η^6-2-Chloro-phenyl)-ethan-1-ol)Cr(CO)$_3$ ((*RS,RS*)-9a). A solution of MeMgBr (2.50 mL, 3 N, 7.50 mmol) was added dropwise to a solution of (*RS*)-**7a** (0.950 g, 3.434 mmol) in THF (20 mL) at −78 °C. After 30 min at −78 °C, the yellow reaction mixture was quenched at −10 °C with aqueous NH_4Cl. The organic layer was washed with water, dried over $MgSO_4$, and volatiles were removed under a vacuum. The residue was purified by flash chromatography (SiO_2, Et_2O/Hx 1−2) to afford the complex (*RS,RS*)-**9a** as a yellow oil (0.892 g, 90%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.35 (dd, 1H, J = 6.4, 1.4 Hz), 4.57 (dd, 1H, J = 6.4, 1.0 Hz), 4.52−4.45 (m, 1H), 4.28 (dt, 1H, J = 6.4, 1.3 Hz), 4.09 (t, 1H, J = 6.1 Hz), 1.67 (d, 1H, J = 3.6 Hz), 1.09 (d, 3H, J = 6.4 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.6, 114.1, 110.9, 92.5, 91.7, 89.6, 89.1, 65.9, 24.2. IR (CH_2Cl_2): 3602, 1975. MS (*m*/*z*): 292(23), 236(10), 208(14), 192(42), 190(100), 172(18), 154(33), 103(48), 77(21), 52(59). HRMS Calcd for $C_{11}H_9ClCrO_4$: 291.9594. Found: 291.9618.

(1-(η^6-2-Chloro-phenyl)-ethan-1-ol)Cr(CO)$_3$ ((*RS,SR*)-9a). Acetic anhydride (15 mL) was added to a DMSO (25 mL) solution of complex (*RS,RS*)-**9a** (2.980 g, 10.205 mmol) and the reaction mixture was stirred for 12 h at room temperature. The solvent was removed under a vacuum. The residue was taken up in ether, washed with $NaHCO_3$ and brine, and dried on $MgSO_4$. Flash chromatography afforded (1-(η^6-2-chloro)-acetophenone)Cr(CO)$_3$ as an orange oil (2.402 g, 80%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.30 (dd, 1H, J = 6.4, 1.1 Hz), 4.40−4.30 (m, 2H), 3.85−3.75 (m, 1H), 2.18 (s, 3H). ^{13}C NMR (C_6D_6, 50 MHz): δ 230.6, 194.4, 150.2, 99.5, 94.3, 94.2, 90.3, 86.3, 26.9. IR (CH_2Cl_2): 1987, 1920, 1683. MS (*m*/*z*): 290(10), 234(11), 206(80), 164(8), 127(10), 103(82), 52(100). HRMS Calcd for $C_{11}H_7ClCrO_4$: 289.9437. Found: 289.9482. The chloroacetophenone complex (1.000 g, 3.448 mmol) was dissolved in ethanol (20 mL), and $NaBH_4$ (65.4 mg, 1.730 mmol) was added portionwise at 0 °C. After 15 min, the reaction mixture was extracted with Et_2O. Flash chromatography (SiO_2, Et_2O/Hx 1−1) gave complex (*RS,SR*)-**9a** as a yellow oil (0.814 g, 81%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.11 (d, 1H, J = 6.5 Hz), 4.55−4.45 (m, 2H), 4.37 (t, 1H, J = 6.4 Hz), 3.94 (t, 1H, J = 6.3 Hz), 1.35 (bs, 1H), 1.26 (d, 3H, J = 6.4 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.6, 114.1, 110.9, 92.5, 91.7, 89.6, 89.1, 65.9, 24.2. IR (CH_2Cl_2): 1975, 1896. MS (*m*/*z*): 292(20), 236(14), 208(10),

190(100), 172(22), 154(30), 103(47), 77(20), 52(57). HRMS Calcd for $C_{11}H_9ClCrO_4$: 291.9594. Found: 291.9632.

(2-(η^6-2-Chloro-phenyl)-pent-4-ene)Cr(CO)$_3$ ((*RS,RS*)-5a). To a solution of complex (*RS,SR*)-**9a** (0.220 g, 0.753 mmol) in CH_2Cl_2 (10 mL) at −78 °C was added $BF_3{\cdot}OEt_2$ (0.150 mL, 1.120 mmol) and allyltrimethylsilane (0.230 mL, 1.441 mmol) at −78 °C. The reaction mixture was stirred overnight while warming from −78 °C to room temperature to afford, after workup, complex (*RS,RS*)-**5a** as a yellow oil (0.221 g, 92%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.55−5.35 (m, 1H), 4.92−4.77 (m, 2H), 4.63 (dd, 1H, J = 6.4, 1.1 Hz), 4.57 (dd, 1H, J = 6.4, 1.1 Hz), 4.35 (dt, 1H, J = 6.3, 1.3 Hz), 4.03 (dt, 1H, J = 6.3, 0.9 Hz), 2.95−2.88 (m, 1H), 2.08−1.92 (m, 1H), 1.90−1.75 (m, 1H), 0.99 (d, 3H, J = 7.0 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.6, 135.1, 128.4, 117.5, 114.0, 92.7, 91.1, 90.9, 88.2, 42.4, 34.3, 18.5. IR (CH_2Cl_2): 1973, 1897. MS (*m/z*): 316(57), 275(4), 232(51), 196(79), 168(14), 145(97), 117(35), 87(46), 77(28), 52(100). HRMS Calcd for $C_{14}H_{13}ClCrO_3$: 315.9958. Found: 315.9911.

Aryl-Radical Cyclization with AIBN/HSnBu$_3$: (η^6(*cis*-3-Methyl-indan-1-ol)Cr(CO)$_3$ (*rac*-10) and (η^6(*trans*-3-Methyl-indan-1-ol)Cr(CO)$_3$ (*rac*-11). To a solution of (*RS, RS*)-**2b** (0.400 g, 1.102 mmol) in benzene (100 mL) was added AIBN (18 mg, 0.110 mmol) and $HSnBu_3$ (0.350 mL, 1.322 mmol). The reaction mixture was brought to reflux (80 °C) and stirred for 2.5 h. The solvent was removed under a vacuum to a afford a yellow oil shown by ^{1}H NMR to consist of a 1:1 mixture of **10** and **11**. The diastereoisomers were readily separated by column chromatography (Et_2O/Hx 1−2, 1−1) to gave **10** as a yellow oil (0.124 g) followed by **11** (0.132 g) as a yellow solid with an overall yield of 82%. Data for (η^6(*cis*-3-methyl-indan-1-ol)Cr(CO)$_3$ (*rac*-**10**). ^{1}H NMR (C_6D_6, 400 MHz): δ 4.86 (d, 1H, J = 6.3 Hz), 4.50 (d, 1H, J = 6.3 Hz), 4.45 (t, 1H, J = 6.1 Hz), 4.40−4.32 (m, 1H), 4.28 (t, 1H, J = 6.2 Hz), 2.62−2.55 (m, 1H), 2.19−2.11 (m, 1H), 1.18−1.09 (m, 2H), 0.93 (d, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6, 100 MHz): δ 232.9, 119.2, 111.4, 92.9, 90.9, 90.3, 88.1, 74.1, 41.0, 37.4, 23.1. IR (Hexane): 1976, 1906. MS (*m/z*): 284(30), 228(4), 198(88), 147(28), 131(33), 91(21), 52(100). HRMS Calcd for $C_{13}H_{12}CrO_4$: 284.0140. Found: 284.0153. Data for (η^6(*trans*-3-methyl-indan-1-ol)Cr(CO)$_3$ (*rac*-**11**). Mp: 115−116 °C (recrd, Et_2O/Hx). ^{1}H NMR (C_6D_6, 400 MHz): δ 4.62−4.55 (m, 2H), 4.45 (t, 1H, J = 6.3 Hz), 4.40−4.30 (m, 1H), 4.26 (t, 1H, J = 6.3 Hz), 2.82 (sextet, 1H, J = 7.5 Hz), 1.68−1.52 (m, 2H), 0.99−0.95 (m, 1H), 0.95 (d, 3H, J = 6.8 Hz). ^{13}C NMR (C_6D_6, 100 MHz): δ 233.2, 119.1, 113.6, 93.0, 89.5, 89.3, 87.3, 73.5, 42.3, 35.1, 17.2. IR (Hexane): 1976, 1904. MS (*m/z*): 284(18), 228(3), 198(68), 147(10), 131(32), 91(15), 52(100). HRMS Calcd for $C_{13}H_{12}CrO_4$: 284.0140. Found: 284.0135.

Aryl-Radical Cyclization Promoted by SmI$_2$: (η^6-(*cis*-3-Hydroxyindan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-12) and (η^6-(*trans*-3-Hydroxyindan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-13). To a solution of SmI_2 (10 mL, 0.1 N in THF, 1.00 mmol) was added dropwise (*RS,RS*)-**6** (0.120 g, 0.250 mmol) in THF (5 mL). Stirring was continued overnight at room temperature. Extraction (Et_2O/NH_4Cl) and column chromatography (SiO_2, Et_2O/Hx 2−1) gave the complexes **12** (18 mg) followed by **13** (20 mg) with 45% overall yield. Data for (η^6-(*cis*-3-hydroxyindan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-**12**). ^{1}H NMR (C_6D_6, 200 MHz): δ 4.89 (d, 1H, J = 6.2 Hz), 4.80 (d, 1H, J = 6.3 Hz), 4.50−4.39 (m, 2H), 4.27 (t, 1H, J = 6.3 Hz), 3.19 (s, 3H), 3.11−3.00 (m, 1H), 2.35−2.25 (m, 1H), 2.29 (d, 2H, J = 6.8 Hz), 2.05 (d, 1H, J = 4.9 Hz,), 1.38 (d, 1H, J = 14.4 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 233.2, 172.1, 116.5, 112.2, 93.1, 91.4, 91.2, 89.3, 74.6, 51.3, 41.2, 39.7, 39.4. IR (CH_2Cl_2): 1967, 1891, 1733. MS (*m/z*): 342(27), 310(1), 258(38), 240(41), 198(79), 128(40), 115(32), 52(100). HRMS Calcd for $C_{15}H_{14}CrO_6$: 342.0195. Found: 342.0200. Data for (η^6-(*trans*-3-hydroxyindan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-**13**). ^{1}H NMR (C_6D_6, 200 MHz): δ 4.82 (d, 1H, J = 6.4 Hz), 4.61 (d, 1H, J = 6.2 Hz), 4.48 (t, 1H, J = 6.2 Hz), 4.38 (d, 1H, J = 5.5 Hz), 4.24 (t, 1H, J = 6.2 Hz), 3.55−3.48 (m, 1H), 3.45 (s, 3H), 2.52 (dd, 1H, J = 16.7, 8.1 Hz), 2.28 (dd, 1H, J = 16.7, 7.1 Hz), 1.94 (dd, 1H, J = 13.8, 7.0 Hz), 1.75−1.65 (m, 1H), 1.3 (bs, 1H). ^{13}C NMR (C_6D_6, 50 MHz): δ 233.5, 172.3, 116.6, 114.5, 93.9, 90.6, 89.9, 88.0, 73.8, 51.4, 41.3, 38.3, 37.5. IR (CH_2Cl_2): 1968, 1891, 1735. MS (*m/z*): 342(6), 314(8), 258(100), 223(5), 198(70), 128(42), 115(37), 52(100). HRMS Calcd for $C_{15}H_{14}CrO_6$: 342.0195. Found: 342.0148.

η^6-(3-Methylene-indan-1-ol)Cr(CO)$_3$ ((*S,S*)-(−)-14). To a suspension of $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol, 5%), PPh_3 (6.6 mg, 0.0250 mmol, 10%) and complex (*S,S*)-(−)-**2a** (80 mg, 0.251 mmol) in CH_3CN (6 mL) was added Et_3N (0.068 mL, 0.502 mmol). The mixture was heated at 80 °C for 4 h, then taken to dryness. Flash chromatography (SiO_2, Et_2O/Hx 9:1) afforded complex (*S,S*)-(−)-**14** as a yellow oil (55 mg, 78%). $[\alpha]_D^{20}$ = −272 (c = 0.34, $CHCl_3$). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.05 (s, 1H), 4.90 (d, 1H, J = 6.2 Hz), 4.85−4.75 (m, 2H), 4.55−4.48 (m, 1H), 4.45−4.35 (m, 2H), 2.70 (ddt, 1H, J = 16.8, 7.2, 2.1 Hz), 2.10 (d, 1H, J = 16.8 Hz), 1.10 (bs, 1H). ^{13}C NMR (C_6D_6, 50 MHz): δ 232.9, 144.2, 114.3, 107.5, 106.8, 92.3, 91.8, 90.3, 85.6, 72.4, 40.4. IR (CH_2Cl_2): 1970, 1896. MS (*m/z*): 282(18), 226(20), 198(96), 180(78), 52(100). HRMS Calcd for $C_{13}H_{10}CrO_4$: 281.9984. Found: 281.9970.

η^6-(1-Methoxy-3-methylene-indan)Cr(CO)$_3$ ((*S,S*)-(−)-15). To a suspension of $Pd(OAc)_2$ (8.5 mg, 0.037 mmol, 5%), PPh_3 (20 mg, 0.075 mmol, 10%), and complex (*S,S*)-(−)-**3a** (0.250 g, 0.753 mmol) in CH_3CN (15 mL) was added Et_3N (0.20 mL, 1.50 mmol). The mixture was stirred at 23 °C for 24 h followed by a flash chromatography (SiO_2, Et_2O/Hx 1−1) to afford the complex (*S,S*)-(−)-**15** as a yellow solid (0.180 g, 85%). Mp: 82 °C. $[\alpha]_D^{20}$ = −437 (c = 0.138, $CHCl_3$). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.05 (dd, 1H, J = 2.7, 1.8 Hz), 4.95 (dd, 1H, J = 5.9, 1.4 Hz), 4.85−4.79 (m, 2H), 4.48−4.32 (m, 2H), 4.25 (dd, 1H, J = 6.4, 1.0 Hz), 2.90 (s, 3H), 2.60 (ddt, 1H, J = 17.0, 6.4, 2.4 Hz), 2.32 (dq, 1H, J = 17.0, 1.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 232.2, 143.7, 111.5, 107.9, 107.1, 92.6, 91.6, 90.6, 85.6, 80.8, 56.6, 36.8. IR (CH_2Cl_2): 1970, 1895. MS (*m/z*): 296(8), 240(4), 212(12), 182(23), 128(6), 52(100). HRMS Calcd for $C_{14}H_{12}CrO_4$: 296.0126. Found: 296.0141.

η^6-(1-Methyl-3-methylene-indan)Cr(CO)$_3$ ((*RS,RS*)-16). To a suspension of $Pd(OAc)_2$ (8.0 mg, 0.033 mmol, 5%), PPh_3 (18 mg, 0.066 mmol, 10%), and complex (*RS,RS*)-**5a** (0.210 g, 0.664 mmol) in CH_3CN (15 mL) was added Et_3N (0.18 mL, 1.32 mmol). The mixture was stirred at 25 °C for 24 h followed by a flash chromatography (SiO_2, Et_2O/Hx 2−1) to afford the complex (*RS,RS*)-**16** as a yellow solid (0.148 g, 80%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.06 (d, 1H, J = 2.6 Hz), 4.94 (d, 1H, J = 6.5 Hz), 4.79 (d, 1H, J = 2.3 Hz), 4.55−4.48 (m, 2H), 4.42 (dt, 1H, J = 6.4, 1.2 Hz), 2.75−2.65 (m, 2H), 1.85−1.70 (m, 1H), 0.69 (d, 3H, J = 7.1 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 233.5, 145.8, 121.5, 107.7, 106.0, 92.8, 90.6, 88.4, 86.8, 38.5, 36.5, 22.7. IR (CH_2Cl_2): 1964, 1888. MS (*m/z*): 280(23), 224(14), 196(100), 144(3), 129(7), 52(99). HRMS Calcd for $C_{14}H_{12}CrO_3$: 280.0191. Found: 280.0146.

General Procedure for the Pd-Catalyzed Carbocyclization Reaction Under CO Pressure. The reactions were carried out in a heavy Schlenk tube fitted with an 8 mm O-ring tap and a rubber septum. To a suspension of $Pd(PPh_3)_4$ and aryl−halide complex in a mixture of CH_3CN and benzene (1:1) was added MeOH. The rubber septum was replaced by an adaptor with a small pressure gauge. The reaction mixture was degased (three freeze−pump−thaw cycles). A total of 4 Bar of CO was pressed onto the mixture, which was then heated with magnetic stirring at 80 °C. Excess CO was vented, and volatiles were evaporated in vacuo. After filtration of the crude reaction mixture on Celite and removal of volatiles under vacuum, flash chromatography afforded the product.

η^6-(3-Methoxyindan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ ((*1S,3S,3aS*)-(+)-18). The general procedure described above was used. $Pd(PPh_3)_4$ (51 mg, 0.0443 mmol, 5%), complex (*S,S*)-(-)-**3a** (0.295 g, 0.887 mmol), Et_3N (0.18 mL, 1.33 mmol), MeOH (0.14 mL, 3.50 mmol), benzene (5 mL), and CH_3CN (5 mL) were heated under CO at 80 °C for 12 h. Workup and column chromatography (SiO_2, Et_2O/Hx 2−1) gave (*1S,3S,3aS*)-(+)-**18** as a yellow oil (0.226 g, 73%). $[\alpha]_D^{20}$ = +12 (c = 0.15, $CHCl_3$). ^{1}H NMR (C_6D_6, 400 MHz): δ 4.98 (d, 1H, J = 6.5 Hz), 4.87 (d, 1H, J = 6.5 Hz), 4.47 (t, 1H, J = 6.5 Hz), 4.29 (t, 1H, J = 6.5 Hz), 3.99 (d, 1H, J = 5.7 Hz), 3.30 (s, 3H), 3.25−

3.15 (m, 1H), 2.88 (s, 3H), 2.42 (d, 2H, J = 7.5 Hz), 2.23 (ddd, 1H, J = 14.5, 7.5, 5.7 Hz), 1.64 (d, 1H, J = 14.5 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 233.2, 171.8, 117.5, 109.6, 93.6, 91.6, 91.0, 89.9, 83.4, 56.6, 51.2, 42.0, 39.8, 36.7. IR (CH_2Cl_2): 1971, 1896, 1732. MS (*m*/*z*): 356(5), 272(18), 240(53), 198(57), 145(87), 52(100). HRMS Calcd for $C_{16}H_{16}CrO_6$: 356.0329. Found: 356.0351.

η^6-(3-(Diphenyl-*t*Bu-silyloxy)-indan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-19). The general procedure described above was used. Pd(PPh_3)$_4$ (22 mg, 0.019 mmol, 10%), complex (*RS*,*RS*)-**4a** (0.105 g, 0.189 mmol), Et_3N (0.053 mL, 0.038 mmol), MeOH (0.05 mL), benzene (3 mL), and CH_3CN (3 mL) were heated under CO at 80 °C for 12h. Workup and column chromatography (SiO_2, Et_2O/Hx 1−3) gave *rac*-**19** as a yellow solid (80 mg, 72%). Mp: 93−94 °C (recrd, Et_2O/Hx). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.72−7.61 (m, 4H,), 7.28−7.15 (m, 6H), 5.00 (d, 1H, J = 5.2 Hz), 4.91 (d, 1H, J = 6.5 Hz), 4.47 (d, 1H, J = 6.2 Hz), 4.41 (td, 1H, J = 6.4, 0.6 Hz), 4.12 (td, 1H, J = 6.3, 0.7 Hz), 3.33 (s, 3H), 3.30−3.15 (m, 1H), 2.61 (d, 2H, J = 7.8 Hz), 2.29 (ddd, 1H, J = 13.8, 7.6, 5.8 Hz), 1.71 (d, 1H, J = 14.0 Hz), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 232.3, 172.2, 136.0, 135.9, 133.5, 132.9, 130.2, 128.0, 127.9, 116.8, 111.0, 93.3, 91.5, 90.7, 89.1, 75.5, 51.8, 42.2, 40.2, 39.5, 26.9, 19.0. IR (CH_2Cl_2): 1967, 1890, 1735. MS (*m*/*z*): 580(14), 496(76), 387(98), 309(18), 240(32), 199(100), 129(37), 115(31), 52(29). HRMS Calcd for $C_{31}H_{32}CrO_6Si$: 580.1373. Found: 580.1389.

η^6-((3-Methyl-indan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-20). The general procedure described above was used. Pd(PPh_3)$_4$ (30 mg, 0.025 mmol, 10%), complex (*RS*,*RS*)-**5a** (80 mg, 0.25 mmol), Et_3N (0.060 mL, 0.475 mmol), MeOH (0.05 mL), benzene (4 mL), and CH_3CN (4 mL) were heated under CO at 80 °C for 15h. Workup and column chromatography (SiO_2, Et_2O/Hx 1−2) gave complex *rac*-**20** as a yellow oil (54 mg, 64%). ^{1}H NMR (C_6D_6, 200 MHz): δ 4.98 (d, 1H, J = 6.3 Hz), 4.60 (d, 1H, J = 6.4 Hz), 4.45−4.35 (m, 2H), 3.32 (s, 3H), 3.32−3.29 (m, 1H), 2.75−2.60 (m, 1H), 2.40−1.95 (m, 3H), 1.00 (dt, 1H, J = 13.5, 2.7 Hz), 0.73 (d, 3H, J = 7.26 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 233.8, 171.4, 119.0, 115.9, 92.3, 91.4, 90.4, 89.4, 51.3, 41.9, 40.0, 38.1, 38.0, 23.0. IR (CH_2Cl_2): 1960, 1878, 1735. MS (*m*/*z*): 340(30), 256(100), 226(12), 196(42), 182(32), 128(18), 52(92). HRMS Calcd for $C_{16}H_{16}CrO_5$: 340.0402. Found 340.0391.

η^6-(2-But-3-enyl-(Benzoic acid methyl ester))Cr(CO)$_3$ ((*RS*)-21). The general procedure described above was used. Pd(PPh_3)$_4$ (0.140 g, 0.121 mmol, 10%), complex (*RS*)-**1a** (0.365 g, 1.208 mmol), Et_3N (0.33 mL, 2.40 mmol), MeOH (0.42 mL), benzene (6 mL), and CH_3CN (6 mL) were heated under CO at 80 °C for 16 h. Workup and column chromatography (SiO_2, Et_2O/Hx 1−4) gave (*RS*)-**21** as an orange oil (0.250 g, 65%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.80−5.65 (m, 1H), 5.67 (d, 1H, J = 6.4 Hz), 5.05−4.90 (m, 2H), 4.65 (t, 1H, J = 6.2 Hz), 4.22 (t, 1H, J = 6.2 Hz), 4.15 (d, 1H, J = 6.4 Hz), 3.52−3.38 (m, 1H), 3.31 (s, 3H), 2.38−2.25 (m, 1H), 2.15−1.98 (m, 2H). ^{13}C NMR (C_6D_6, 100 MHz): δ 231.7, 165.8, 137.2, 115.8, 115.0, 96.6, 95.3, 91.7, 90.0, 87.8, 52.0,36.0, 34.0. IR (CH_2Cl_2): 1977, 1905, 1724. MS (*m*/*z*): 326(22), 314(5), 262(2), 242(83), 201(52), 171(21), 129(4), 91(8), 52(100). HRMS Calcd for $C_{15}H_{14}CrO_5$: 326.0246. Found 326.0250.

(η^6-3-Methoxyindan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-22). The general procedure described above was used. Pd(PPh_3)$_4$ (33 mg, 0.0282 mmol, 5%), complex (*RS*,*SR*)-**3a** (0.188 g, 0.565 mmol), Et_3N (0.16 mL, 1.13 mmol), MeOH (0.11 mL), benzene (5 mL), and CH_3CN (5 mL) were heated under CO at 80 °C for 16 h. Workup and column chromatography (SiO_2, Et_2O/Hx 1−1) gave *rac*-**22** as a yellow oil (0.107 g, 50%). ^{1}H NMR (C_6D_6, 200 MHz): δ 5.08 (d, 1H, J = 6.5 Hz), 4.66 (d, 1H, J = 6.1 Hz), 4.51 (td, 1H, J = 6.1, 1.0 Hz), 4.24 (td, 1H, J = 6.3, 1.0 Hz), 4.14 (dd, 1H, J = 8.2, 6.9 Hz), 3.27 (s, 3H), 3.27−3.18 (m, 1H), 3.03 (s, 3H), 1.98−1.85 (m, 1H), 1.93 (d, 2H, J = 7.5 Hz), 1.70 (ddd, 1H, J = 12.8, 6.7, 1.0 Hz). ^{13}C NMR (C_6D_6, 50 MHz): δ 233.3, 171.3, 115.7, 113.1, 93.5, 90.2, 89.0, 86.9, 80.3, 57.3, 51.3, 40.2, 38.2, 37.1. HRMS Calcd for $C_{16}H_{16}CrO_6$: 356.0329. Found: 356.0348.

(η^6-3-Methyl-indan-1-yl)acetic acid methyl ester)Cr(CO)$_3$ (*rac*-23). The general procedure described above was used. Pd(PPh_3)$_4$ (56 mg, 0.0475 mmol, 10%), complex (*RS*,*SR*)-**5a** (0.150 g, 0.475 mmol), Et_3N (0.12 mL, 0.95 mmol), MeOH (0.10 mL), benzene (5 mL), and CH_3CN (5 mL) were heated under CO at 80 °C for 16 h. Workup and column chromatography (SiO_2, Et_2O/Hx 1−3) gave *rac*-**23** as a yellow oil (0.100 g, 60%). ^{1}H NMR (C_6D_6, 400 MHz): δ 4.72−4.65 (m, 2H), 4.63 (t, 1H, J = 6.4 Hz), 4.27 (t, 1H, J = 6.0 Hz), 3.33 (s, 3H), 3.20−3.05 (m, 1H), 2.45−3.32 (m, 1H), 1.99 (d, 2H, J = 7.6 Hz), 1.80−1.65 (m, 1H), 1.51 (dd, 1H, J = 13.0, 6.8 Hz), 1.00 (d, 3H, J = 6.4 Hz). ^{13}C NMR (C_6D_6, 100 MHz): δ 233.9, 171.3, 118.4, 118.3, 94.1, 90.6, 88.6, 86.9, 51.1, 39.4, 39.3, 38.8, 35.6, 18.0. IR (CH_2Cl_2): 1963, 1883, 1734. MS (*m*/*z*): 340(20), 256(100), 212(5), 196(38), 128(11), 52(85). HRMS Calcd for $C_{16}H_{16}CrO_5$: 340.0403. Found: 340.0406.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for complexes **2a**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **18**, **19**, **20**, **22**, and **23**; ORTEP diagram and table with selected bond lengths (Å) and bond angles and torsional angles (deg) for complex *rac*-**19**; crystallographic data for the compound **19** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-100862 (see ref 9a). This material is available free of charge via the Internet at http://pubs.acs.org.

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