Conformationally Constrained Diphosphines Derived from (η^6-(*S*)-1-(dimethylamino)indane)Cr(CO)$_3$: Synthesis and Application in Enantioselective Hydrogenation

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Three new enantiopure diphosphine ligands have been prepared starting from [(η^6-(1-dimethylamino)indane)Cr(CO)$_3$] by means of a stereoselective synthetic strategy involving highly diastereoselective complexation of the Cr(CO)$_3$ moiety to (*S*)-(1-dimethylamino)indane, regioselective substitution in the 7-position with the PPh$_2$ group, and, after exchange of the amino group for a chloro substituent with chloroformic esters, introduction of a PR$_2$ group (R = Ph, *t*-Bu, Cy) in the benzylic position. The stereochemical course of the synthesis has been confirmed by the X-ray determination of the molecular structure of one intermediate and of one of the three ligands. The ligands have been tested in the rhodium-promoted enantioselective hydrogenation of methyl (*Z*)-*N*-acetamidocinnamate and dimethyl itaconate. Enantiomeric excesses ranging from 9 to 88% ee have been obtained, depending on the nature of the R substituent on the ligand, with the donor group combination *o*-PPh$_2$/α-PCy$_2$ **(*S*,*R*p)-6c** outperforming the other two. The new ligands, which bear the coordinating teeth on the stiff backbone provided by the indane framework, compare well with the parent conformationally unlocked "Daniphos" ligands: in the hydrogenation of dimethyl itaconate the new ligand **(*S*,*R*p)-6c** provides better results as to conversion and enantioselectivity compared to the analogous acyclic ligand.

Introduction

The asymmetric catalytic synthesis of enantiopure compounds is of primary importance in synthetic organic chemistry, in view of the industrial production of specialities and fine chemicals.[1] Among the different catalytic processes, hydrogenations are by far the predominant transformations that have been successfully developed to industrial application.[1k] Catalytic hydrogenation of unsaturated organic compounds[1,2] is a clean reaction. Frequently the reaction proceeds quantitatively without formation of side products and there is no waste except the trace amount of catalyst. Thus, in terms of ecology and atom economy, "catalytic hydrogenation comes the closest to being an ideal reaction that is extensively practiced both industrially and academically".[3]

Metal catalysts usually consist of a metal center and a coordinated ligand which provides the source of the stereochemical information required for the metal-mediated transformation to proceed in a stereoselective fashion. It is well established that the efficiency (activity plus selectivity) of a homogeneous metal catalyst depends on a variety of parameters and, among these, on a subtle electronic, geometric, and steric interplay between the ligand(s) and the metal center. Due to this complexity and to the often very pronounced product specificity, the principle of "variation and selection"[4] is generally applied in the development of new powerful catalysts by researchers: the organic ligand attached to the metal is varied and the new complex is tested (screened). To speed up discoveries, *modular ligand architectures* are highly desirable, because they accelerate the systematic variation and optimization of the

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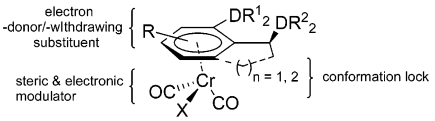
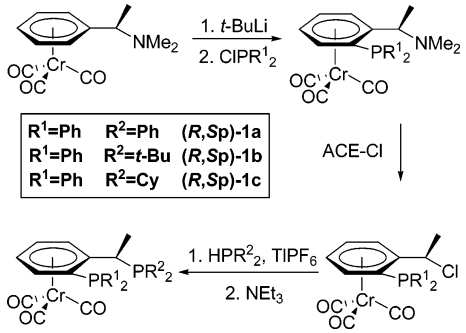
Chart 1. Accessibility of Modular Ligand Architecture Based on (η^6-Arene)chromium Tricarbonyl Complexes



Scheme 1. General Synthetic Strategy for the Preparation of "Daniphos"-like Diphosphines



ligand stucture.[5] We recently reported a stereoselective synthetic strategy[6] through which a modular ligand architecture is now accessible based on (η^6-arene)-chromium tricarbonyl complexes (Chart 1).

The ligands[7] are prepared by starting from commercially available optically pure benzylamines and are characterized by the presence of a stereogenic plane and a stereocenter. Planar chirality is introduced by means of diastereoselective directed ortho metalation[8] (DOM[8d]) and subsequent electrophilic substitution on the arene ring.[9] Central chirality is preserved through the stereoselective replacement of the dimethylamino group for a chloride with chloroethyl chloroformate (ACE-Cl) and the subsequent stereoselective nucleophilic substitution of the chloro substituent for a different nucleophile (Scheme 1).[6] On the basis of this approach, mono- and bidentate ligands suitable for application in enantioselective homogeneous catalysis have been prepared and exploited in diverse catalytic applications.[10] Because transition-metal complexes associated with chiral phosphorus ligands[11] are the dominant choice of catalysts for asymmetric hydrogenation,[12] a range of C_1-symmetric diphosphines (from now on they will be generally referred to as the Daniphos type of ligands) have been synthesized and successfully applied in the rhodium-promoted asymmetric homogeneous hydrogenation of classical substrates such as α-enamides and itaconates:[13] a small focused library of ligands has been created by independently modifying the nature of the R^1/R^2 substituents at phosphorus in order to vary the electronic and steric properties of the donor teeth, and the influence of such properties on the catalytic performances of the corresponding metal complexes has been assessed.

One more parameter to take into account in the design of a ligand for metal catalysis is conformational flexibility: in the formation of transition-metal complexes, the flexibility of the ethyl side chain of Daniphos diphosphines—in particular, the fact that the whole unit can rotate about the $C_{ipso}-C_\alpha$ single bond—contributes in fact to the necessary ligand adjustment. It also allows the catalytic system to adapt to changing oxidation states, geometries, and substitution patterns which typically occur during the course of a catalytic cycle. Depending on the type of ligand, however, conformational flexibility can translate into conformational ambiguity and reduced enantioselectivity, if several minimum energy conformations are accessible, thus increasing the number of reactive conformers of the catalytic active species.

Therefore, in addition to an investigation into steric and electronic effects, it seemed of interest to us to study the influence of a reduced conformational flexibility on activity and selectivity ("stiff" versus "flexible" ligand backbones) by changing the mobile side chain of Daniphos-type ligands to a much less flexible arene-fused five-membered ring, such as the one provided by (1-dimethylamino)indane. When it is complexed to the $Cr(CO)_3$ moiety, the latter ligand still provides the amino functionality on a "benzylic" carbon, which is strategic for further functionalization. A similar investigation has been carried out by Weissensteiner on the ferrocenyldiphosphines counterpart.[14]

Results and Discussion

Diastereoselective Complexation. Prior to the complexation to the $Cr(CO)_3$ moiety, (*S*)-1-aminoindane has been reductively methylated with formaldehyde and formic acid by means of the Eschweiler–Clarke proce-

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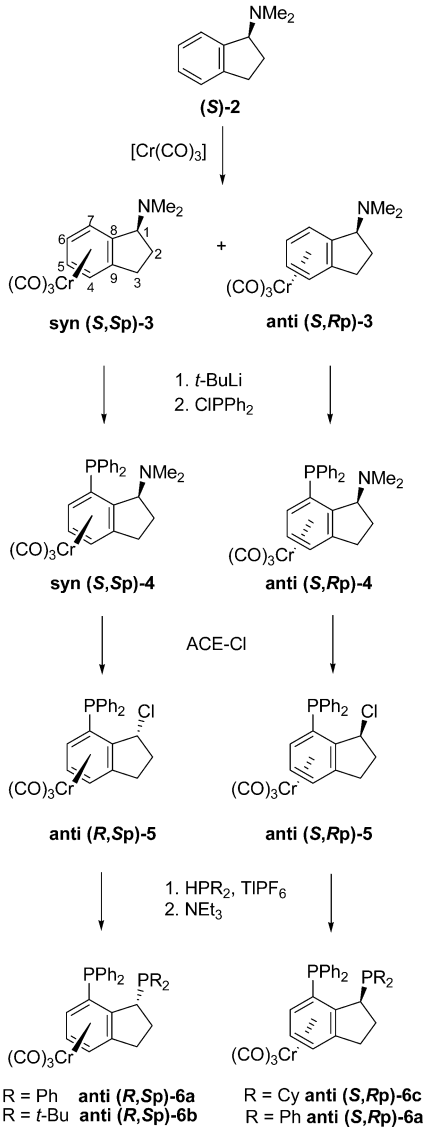
Scheme 2. Synthesis of [(η^6-indane)Cr(CO)$_3$]-Based Diphosphines: Stereochemical Relationships



dure[15] to give (*S*)-(1-dimethylamino)indane (**(*S*)-2**) in 64% yield. Protection of the amino group is necessary in order to reduce its coordinating ability toward chromium, which might lead to incomplete complex formation.

The two faces of the arene in **(*S*)-2** are diastereotopic, and diastereomeric complexes arise from the coordination of the Cr(CO)$_3$ fragment to either of these two faces (Scheme 2). Diastereoselective complexation[16] of (*S*)- (1-dimethylamino)indane (**(*S*)-2**) has been initially carried out using the easily accessible [Cr(CO)$_6$] (Table 1, entry 1).

Under the conditions described by Mahaffy and Pauson[17] (dibutyl ether/THF 8/1, 140 °C, 66 h), {[η^6-(*S*)-(1-dimethylamino)indane]Cr(CO)$_3$} has been obtained as a mixture of the ***anti*-(*S*,*R*p)-3**[18] and ***syn*-(*S*,*S*p)-3** isomers in a 58/42 ratio (35% isolated yield), with the organometallic fragment placed anti or syn to the dimethylamino group, respectively. Assignment of the anti and syn configurations was made by means of the NMR spectra (see below), and the diastereomeric ratio was established through integration of the peaks relative to the two species. Attempts to conveniently separate the two diastereoisomers by flash chromatography were not successful. Fractional crystallization failed to give the two diastereoisomers in acceptable diastereomeric purity and yield. Although very poor, the observed diastereoselectivity in favor of the anti isomer is likely the result of a preference of the Cr(CO)$_3$ moiety for the least hindered face of the arene opposite the $-NMe_2$ group under the thermodynamic conditions of the complexation.

Better diastereoselectivities were achieved when complexation of **(*S*)-2** was carried out using Kündig's reagent [(naphthalene)Cr(CO)$_3$].[19] The latter is a good starting material for the mild synthesis of other (η^6-arene)chromium tricarbonyl compounds via Cr(CO)$_3$-fragment transfer. In marked contrast to the very inert benzene−chromium bond, the naphthalene−chromium bond, although thermally stable, is labile. The lability appears to be a consequence of the ability of the naphthalene ligand to undergo facile $\eta^6 \rightarrow \eta^4$ slippage, freeing a coordination site for an incoming ligand.[19a] The first attempt at diastereoselective complexation using Kündig's reagent was carried out in pure THF (Table 1, entry 2): ***anti*-(*S*,*R*p)-3** and ***syn*-(*S*,*S*p)-3** formed in equal amounts. In addition, no diastereoselectivity was observed by Kündig in the complexation of 1-hydroxycyclobutabenzene under analogous reaction conditions.[20] In diethyl ether (Table 1, entry 3) a dramatic improvement in selectivity was observed, although at the price of a lower yield and longer reaction time. This result suggests that the particular solvent used in the complexation can have a direct impact on the diastereomeric ratio: THF must compete with the substrate nitrogen atom for chromium coordination sites, negating the intramolecular heteroatom delivery of the Cr(CO)$_3$ fragment that would result in a facially selective complexation. In less coordinating Et$_2$O, the chromium atom is able to bind to the benzylic nitrogen of (*S*)-(1-dimethylamino)indane, which delivers the Cr(CO)$_3$ fragment to the syn face of the arene, to give exclusively the kinetically favored syn complex. To reduce the reaction time and increase the yield, the complexation was carried out in a higher boiling less coordinating solvent, dibutyl ether (Table 1, entry 4). The excellent diastereoselectivity was retained, but the yield was still not satisfying. The best compromise among diastereoselectivity, yield, and reaction time was achieved by carrying out the reaction in dibutyl ether in the presence of a small amount of THF as catalyst to accelerate the exchange naphthalene−(*S*)-(1-dimethylamino)indane

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Table 1. Conditions and Results of the Diastereoselective Complexation of (*S*)-2 to the [Cr(CO)$_3$] Fragment

entry	[Cr]	solvent	*T* (°C)	*t* (h)	syn/anti	yield (%)
1	[Cr(CO)$_6$]	*n*-Bu$_2$O/THF	140	66	42/58	35
2	[(η^6-naphthalene)Cr(CO)$_3$]	THF	66	20	~50/50	75
3	[(η^6-naphthalene)Cr(CO)$_3$]	Et$_2$O	35	96	≥99/1	22
4	[(η^6-naphthalene)Cr(CO)$_3$]	*n*-Bu$_2$O	75	22	≥99/1	35
5	[(η^6-naphthalene)Cr(CO)$_3$][a]	*n*-Bu$_2$O	75	91	94/6	91

[a] The mixture contained 1.2 equiv of THF with regard to [Cr].

(Table 1, entry 5).[19a,21] Pure ***syn*-(*S*,*S*p)-3** could be obtained by flash chromatography in 91% isolated yield.

Assignment of the syn and anti configurations was made on the basis of the ^{1}H NMR spectra and later confirmed by the X-ray structure of the species derived from ortho lithiation of ***syn*-(*S*,*S*p)-3** and subsequent electrophilic quenching with diphenylphosphine. The complexation of the Cr(CO)$_3$ fragment causes a large upfield shift of the aromatic ring proton resonances (ca. 2.5 ppm) and a smaller upfield shift of the alicyclic ring and dimethylamino proton resonances. In the syn complex **(*S*,*S*p)-3**, the pattern of proton−proton coupling in the five-membered ring of (*S*)-(1-dimethylamino)-indane is retained (see Scheme 2 for numbering of atoms). The observed coupling for H(1) in (*S*)-(1-dimethylamino)indane is 7.0 Hz, giving rise to a triplet suggesting an almost equal coupling to both H(2) atoms; in the corresponding syn complex the coupling constants are 11.0 and 7.0 Hz. On the basis of the size of the coupling constants and previous analysis of the puckering of the alicyclic ring in 1-indanol and (1-indanol)Cr(CO)$_3$ derivatives,[22] it is possible to assume that the preferred conformations in solution of (*S*)-(1-dimethylamino)indane (**(*S*)-2**) and *syn*-[η^6-(*S*,*S*)-(1-dimethylamino)indane]tricarbonylchromium(0) (**(*S*,*S*p)-3**) have a pseudoequatorial −NMe$_2$ group. In the anti complex **(*S*,*R*p)-3**, instead, H(1) is a doublet with a coupling constant of 7.6 Hz. No coupling is observed to the other H(2) proton. This would suggest a preferred conformation in solution with a pseudoaxial −NMe$_2$ group. The major isomer obtained from the arene exchange reaction has the chemical shift of the aromatic proton signals in the order H(6) < H(4) < H(5) < H(7), while the order of chemical shifts for the minor isomer is H(6) < H(5) < H(4) < H(7). The spread of the δ values in the latter is slightly smaller than in the former. The preferred Cr(CO)$_3$ conformation is thought to be an important factor affecting chemical shifts of aromatic protons in (η^6-arene)Cr(CO)$_3$, and in 1-substituted indanes larger chemical shifts are a characteristic feature of the syn diastereoisomer.[23] The Cr(CO)$_3$ fragment predominantly adopts a conformation in which adverse interactions with the syn substituent are minimized. H(5) and H(7), being eclipsed by a Cr−CO vector in the preferred conformation, are deshielded relative to the other arene protons. For comparison, it is worth mentioning that, in the case of 1-methoxyindane, both *syn*- and *anti*-[(1-methoxyindane)Cr(CO)$_3$] adopt staggered conformations in the solid state, thus suggesting that the wider splitting of the aromatic proton chemical shifts might reflect anisotropic effects due to the substituent rather than conformational effects.[23]

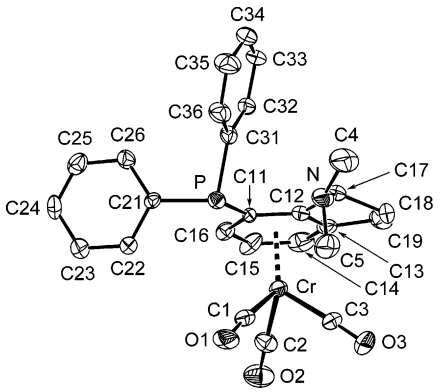

Figure 1. Molecular structure and crystallographic numbering scheme for ***syn*-(*S*,*S*p)-4** (PLATON representation). Ellipsoids are scaled to enclose 30% probability.

Directed Ortho Metalation. *syn*-[η^6-(*S*,*S*p)-1-(dimethylamino)-7-(diphenylphosphino)indane]Cr(CO)$_3$ (**-(*S*,*S*p)-4**) was prepared from *syn*-[η^6-(*S*)-(1-dimethylamino)indane]Cr(CO)$_3$ (**(*S*,*S*p)-3**) by reaction with *t*-BuLi and subsequent quenching with ClPPh$_2$ (Scheme 2). The reaction was highly regioselective, and only the regioisomer in which lithiation at the 7-position had occurred could be detected in the ^{1}H NMR spectrum. This high selectivity most likely arises from a combination of inductive effects and specific coordination of the base (lithium counterion) to the dimethylamino group. Crystals suitable for an X-ray structure determination were grown from a layered mixture of acetone and hexane at −30 °C. The solid-state structure confirmed the endo configuration and the site of lithiation (Figure 1). The X-ray structure of the complex ***syn*-(*S*,*S*p)-4** shows that the five-membered ring is slightly bent, with carbon C(18) pointing toward the Cr(CO)$_3$ group. The dimethylamino group on the cyclopentane ring is in a pseudoequatorial position. The benzene ring shows no deviation from planarity. The Cr−C(aromatic ring) distances range from 2.17 to 2.27 Å. The (benzene)Cr(CO)$_3$ group adopts an almost eclipsed conformation, with one CO nearly aligned with the C(11)−P bond. This arrangement forces the other two CO groups away from the dimethylamino group and the C(18) carbon, which is placed below the molecular plane defined by the arene ring. Likewise, the face-and-edge orientation of the two phosphorus phenyl substituents prevents severe steric hindrance with the Cr(CO)$_3$ tripod and the dimethylamino group.

Directed ortho metalation with *t*-BuLi and subsequent electrophilic quenching with chlorodiphenylphosphine of a mixture of ***syn*-(*S*,*S*p)-3** and ***anti*-(*S*,*R*p)-3** gave, in addition to ***syn*-(*S*,*S*p)-4**, only *anti*-[η^6-(*S*,*R*)-(1-dimethylamino)-7-diphenylphosphinoindane]tricarbonylchromium(0) (***anti*-(*S*,*R*p)-4**), thus indicating that lithi-

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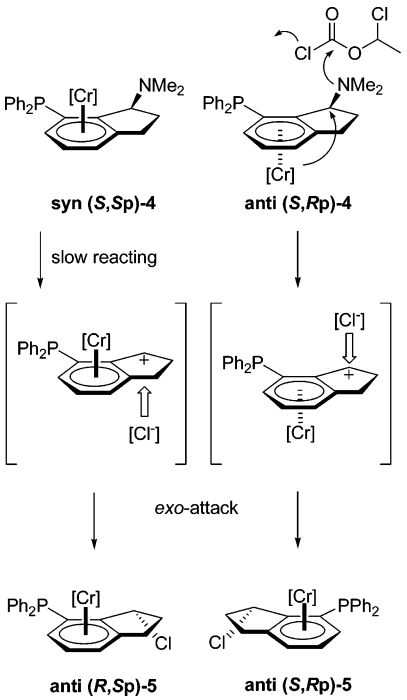
Scheme 3. Likely Mechanism for Substitution of −NMe$_2$ for −Cl with Chloroethyl Chloroformate (ACE-Cl)



ation is highly regioselective even in the case of the exo complex. The site of lithiation could be reasonably assigned on the basis of homo- and heterocorrelated bidimensional NMR spectra and comparison with the spectra of the corresponding syn complex. This experiment was carried out to test whether separation of the syn and anti diastereoisomers by means of conventional flash chromatography could be performed at this stage, since it had not been possible after complexation. Although some anti complex, which is the less polar of the two diastereoisomers, could be isolated in diastereomerically pure form for characterization and further functionalization, flash chromatography failed to provide a feasible and convenient separation of the two complexes.

Substitution of −NMe$_2$ for −Cl. *anti*-[η^6-(*R*,*S*p)-1-chloro-7-(diphenylphosphino)indane]tricarbonylchromium(0) (**(*R*,*S*p)-5**) and *anti*-[η^6-(*S*,*R*p)-1-chloro-7-(diphenylphosphino)indane]tricarbonylchromium(0) (**(*S*,*R*p)-5**) were prepared from ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-4,** respectively, by reaction with ethyl chloroformate. The reaction proceeds according to the mechanism depicted in Scheme 3, most likely through the formation of a transient or intermediate cationic species.

The Cr(CO)$_3$ moiety has been defined as "hermaphroditic" because of its ability to stabilize both benzylic anions and cations.[24] A wealth of implicit structural information on Cr(CO)$_3$-complexed benzylic cations is available.[25] Cr(CO)$_3$ complexation of a benzylic halide or alcohol leads to increased rates of solvolysis.[24] Such substitution reactions occur with retention of stereochemistry at the benzylic position. The stabilization of the benzylic positive charge is ascribed to a neighboring group participation of the chromium center: that is, a charge donation from Cr(CO)$_3$ occupied orbitals into the formally empty p-atomic-like orbitals at the methylene carbon.[26a] Distortion of the benzylic ligand away from planarity and shifting of the chromium away from the center of the aromatic ring increases the spatial overlap between these orbitals, leading to further stabilization. To still correspond to a formal 18-electron species, the bonding between the metal and the arene should become η^7. From this bonding picture it should be expected that these cations incorporate a substantial amount of exocyclic double-bond character. The computed energy barrier to rotation around the $C_{ipso}-CH_2$ bond in the [(toluene)Cr(CO)$_3$] derived benzylic carbocation is 45.4 kcal mol^{-1}, higher than in the corresponding benzylic anion. ^{1}H and ^{13}C NMR experiments demonstrated hindered rotation about the exocyclic carbon−carbon bond in (1-*p*-tolylethyl)- and (*p*-tolylmethyl)tricarbonylchromium cations.[27] This means that, once formed, the benzylic carbocation is configurationally stable. As a consequence, if the leaving group was expulsed while positioned anti to the chromium center and the nucleophilic attack occurs from the exo face (the endo face being well protected by the bulky Cr(CO)$_3$ group), a double-inversion mechanism takes place, resulting in an overall retention of configuration.

The presence of a ring fused to the arene as in ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-4** provides one more opportunity for stereocontrol of the reaction outcome compared to the acyclic systems. A stabilized, cationic intermediate, generated at the benzylic position, has only one possible conformation, as a consequence of the constraints of the ring. Nucleophilic attack on such intermediates occurs exclusively from the exo (uncomplexed) face, and this explains why the diastereoisomers ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-4** provide ***anti*-(*R*,*S*p)-5** and ***anti*-(*S*,*R*p)-5**, respectively, which are enantiomers.

In order for the chromium tricarbonyl moiety to participate as a neighboring group in the stabilization of the buildup of positive charge in the transition state of these reactions, certain stereoelectronic requirements must be met. Maximum overlap between the d orbitals on chromium and the σ^* orbital of the leaving group is best achieved when the nucleofuge lies anti to chromium (Scheme 3). This was confirmed by an experiment in which an equimolecular mixture of ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-4** in THF was treated with chloroethyl chloroformate. The course of the reaction was followed by ^{31}P NMR and revealed that reaction of the anti diastereoisomer was faster than that of the syn one. Unfortunately, under the reaction conditions, the difference in the rates of reaction was not high enough to allow a kinetic resolution of the two diastereoisomeric substrates. This experiment provides further support in favor of the "exo attack", in that only one phosphorus signal for the product enantiomers was detected when the reaction was complete. A similar behavior had been observed when a mixture of *exo*- and *endo*-(1-hydroxyindane)Cr(CO)$_3$ in acetonitrile was treated with sulfuric acid in a dropwise manner.[28] When the course of the

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Table 2. ^{31}P NMR Data of (η^6-indane)Cr(CO)$_3$-Based Diphosphines and of Analogous Acyclic Daniphos Ligands

	$\delta(^{31}P)$ (ppm)[a]					$\delta(^{31}P)$ (ppm)[b,c]		
ligand	*o*-PPh$_2$	α-PR$_2$	$^4J_{PP}$ (Hz)	R	ligand	*o*-PPh$_2$	α-PR$_2$	$^4J_{PP}$ (Hz)
(*R*,*S*p)-6a	−16.02	6.56	58.0	Ph	**(*R*,*S*p)-1a**	−19.99	7.88	20.1
(*S*,*R*p)-6c	−18.80	16.71	64.1	Cy	**(*R*,*S*p)-1c**	−21.21	15.12	45.8
(*R*,*S*p)-6b	−19.13	50.05	89.7	*t*-Bu	**(*R*,*S*p)-1b**	−21.80	48.79	67.8

[a] NMR spectra recorded in C_6D_6. [b] NMR spectra recorded in $CDCl_3$. [c] These data, which are provided for comparison, have been taken from ref 13.

reaction was followed by thin-layer chromatography, the total disappearance of the exo alcohol and its conversion into the corresponding amide was observed, while the endo epimer remained largely unchanged.

Despite these experimental observations, density functional theory calculations carried out by Merlic and Houk indicate that the strongly stabilizing effect of chromium tricarbonyl on benzylic cations is extremely sensitive to skeletal alterations.[26b] Secondary and tertiary cations receive much less stabilization from the chromium moiety than the primary benzyl cation, due to the fact that alkyl substituents are electron releasing and thus stabilizing. In the 1-indanyl cation complex, the stabilizing effect of the metal would be expected to be reduced relative to the primary benzyl cation because the former is secondary. Furthermore, tying the cationic center of 1-indane into a ring limits its tilt toward the metal, which is expected in order to allow for an effective overlap between the metal d orbitals and the cationic center. These calculations suggest that in reactions where the chromium-bound benzylic cation is conformationally restricted, the metal is primarily playing a steric role rather than one of direct participation. Whether electronic or steric, the influence of the Cr(CO)$_3$ tripod renders the replacement of the dimethylamino group by the chloride a stereospecific reaction.

Substitution of −Cl for −PR$_2$: Synthesis of Diphosphines. Reaction of either ***anti*-(*R*,*S*p)-5** or ***anti*-(*S*,*R*p)-5** with a secondary phosphine in the presence of $TlPF_6$ in acetone gave access to the diphosphines **(*R*,*S*p)-6a**, **(*R*,*S*p)-6b**, **(*S*,*R*p)-6c**, and **(*S*,*R*p)-6a** according to Scheme 2. Each diphosphine was obtained as a single diastereomer, and no trace (within the detection limits of NMR) was detected of the isomeric product with opposite configuration of the stereogenic center.

All ligands display in the ^{31}P NMR spectra the expected pair of doublets arising from a simple AX system: the resonances of the α-PR$_2$ group show a downfield shift with increasing steric crowding at phosphorus due to changes in the hybridization of phosphorus (Table 2).[29] The large ^4J phosphorus−phosphorus coupling constants, which range from 58 to 90 Hz in deuterated benzene, are indicative of a preferred time-averaged conformation in solution in which the C$_\alpha$−P bond is nearly perpendicular to the 1,3-bis(phosphino)allylic fragment (PC$_o$=C$_{ipso}$C$_\alpha$P).[30] It is known that for such fragments the absolute value for the ^4J allylic coupling reaches a maximum when the vector of the bond connecting the allylic substituent (here C$_\alpha$−P) lies in a plane perpendicular to the allylic

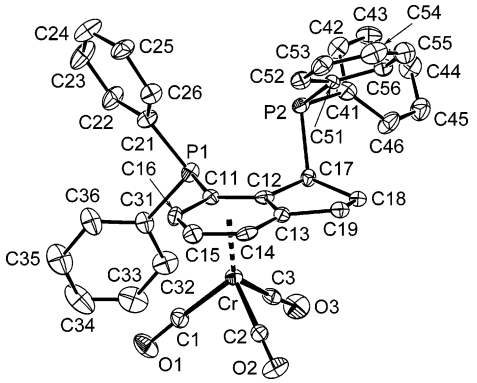

Figure 2. Molecular structure and crystallographic numbering scheme for **(*S*,*R*p)-6a** (PLATON representation). Ellipsoids are scaled to enclose 30% probability.

moiety. The large value of ^4J(P−P) also reflects the relative orientation of the two phosphorus lone pairs which, in the preferred time averaged conformation of the ligands, should be nearly parallel and face each other.[31] The larger values observed for the derivatives bearing bulky cyclohexyl and *tert*-butyl groups, compared to those which only possess phenyl substituents, also reflect the restricted conformational freedom those substituents bring about.[32] The ^4J(P−P) values are also greater than those of the acyclic parent diphosphines **(*R*,*S*p)-1a**, **(*R*,*S*p)-1b**, and **(*R*,*S*p)-1c**,[10b] thus confirming the increased conformational constraint imposed upon the ligands by the indane framework.

The molecular structure of the ligand **(*S*,*R*p)-6a** was determined by X-ray diffraction. Crystals for X-ray determination were obtained from a nonracemic but enantiomerically enriched sample of ligand **(*S*,*R*p)-6a** dissolved in deuterated benzene (NMR sample) and include an equimolar amount of disordered solvent. Despite residuals, the X-ray determination (Figure 2, Table 3) allowed us to confirm the relative configuration of the ligand and, together with previous results, the stereochemical course of the synthesis of the diphosphines.

According to what was reported above, reaction of an equimolecular mixture of ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-4** in THF with chloroethyl chloroformate produces a racemic mixture of the chloro derivatives. This is only possible if both endo and exo dimethylamino derivatives react through an S$_N$1 + "exo" attack mechanism or the endo complex via an S$_N$2 and the exo complex via an S$_N$1 + "exo" attack mechanism, respec-

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Table 3. Crystallographic Data for *syn*-[η^6-(*S,S*p)-1-(dimethylamino)-7-(diphenylphosphino)indane]Cr(CO)$_3$ (*syn*-(*S,S*p)-4) and *anti*-[η^6-(*S,R*p)-1,7-bis(diphenylphosphino)indane]Cr(CO)$_3$ (*anti*-(*S,R*p)-6a)

	***syn*-(*S,S*p)-4**	***anti*-(*S,R*p)-6a**
empirical formula	$C_{26}H_{24}CrNO_3P$	$C_{36}H_{28}CrO_3P_2 \cdot C_6D_6$
fw	481.43	622.56·78.06
temp (K)	253(2)	228(2)
wavelength (Å)	0.710 70	0.710 73
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
unit cell dimens		
a (Å)	10.399(3)	10.7821(17)
b (Å)	12.562(5)	13.220(7)
c (Å)	18.042(5)	12.5118(18)
α (deg)	90	90
β (deg)	90	100.691(12)
γ (deg)	90	90
V (Å^3)	2356.9(13)	1752.4(10)
Z	4	2
calcd density (Mg m^{-3})	1.357	1.328
abs coeff (mm^{-1})	0.581	0.457
F(000)	1000	728
cryst size (mm)	0.48 × 0.40 × 0.20	0.64 × 0.48 × 0.44
θ range for data collecn (deg)	$3.24 < \theta < 25.10$	$2.26 < \theta < 25.10$
index ranges	$0 \le h \le 12$ $-14 \le k \le 14$ $-21 \le l \le 21$	$-12 \le h \le 12$ $-15 \le k \le 15$ $-14 \le l \le 14$
no. of rflns collected	6798	7476
no. of indep rflns	4184 (R(int) = 0.0740)	6225 (R(int) = 0.0999)
abs cor	empirical	empirical
max/min transmissn	1.000 and 0.938	0.8243 and 0.7587
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	4184/0/289	6225/1/391
goodness of fit on F^2	1.061	1.007
final R indices ($I > 2\sigma(I)$)	R1 = 0.0704, wR2 = 0.1052	R1 = 0.1000, wR2 = 0.2259
R indices (all data)	R1 = 0.1411, wR2 = 0.1156	R1 = 0.1656, wR2 = 0.2592
abs structure param	0.04(4)	0.00(6)
largest diff peak/hole (e Å^{-3})	0.469/0.269	1.013/−0.604

tively. Enantiomeric exo diphosphines can then only arise from such a racemic mixture of ***anti*-(*R,S*p)-5** and ***anti*-(*S,R*p)-5** if a S$_N$1 + "exo" attack mechanism is taking place in the second step of the synthesis (if no source of additional chiral information is present in the reaction environment, enantiomers must react according to the same mechanism).

Although an S$_N$2 mechanism cannot be ruled out in the formation of the ***anti*-(*R,S*p)-5** (diastereoisomers can react according to different mechanisms!), it is highly likely that the same S$_N$1 + "exo" attack mechanism, which is operative in the nucleophilic substitutions leading to the desired diphosphines, takes place in the formation of the chloro derivatives.

The overall structural features of the compound **(*S,R*p)-6a** are similar to those of its dimethylamino−dimethylphosphino precursor.

The five-membered ring is slightly bent, with carbon C(18) pointing toward the Cr(CO)$_3$ group. However, this effect is less pronounced, as indicated by the C(13)−C(12)−C(17)−C(18) dihedral angle, which is 15.2° for this molecule and 20.5° for ***syn*-(*S,S*p)-4**. The benzene ring shows a very small deviation from planarity (dihedral angles ranging from 0.1 to 3.5°), which might arise from the steric demand imposed upon the molecule by the two diphenylphosphino groups. To accommodate the benzylic phosphino group, a rotation of nearly 53° around the C(11)−P(1) bond away from the inner part of the molecule takes place compared to ***syn*-(*S,S*p)-4**. This rotation places one of the phenyl groups closer to the Cr(CO)$_3$ tripod. In addition, the P(2)−C(17) bond is nearly perpendicular to the plane of the arene ring, with a torsion angle P(2)−C(17)−C(12)−C(13) of 111.99°. The four phenyl groups are arranged in a edge-and-face fashion. The phosphino groups are already well preorganized for complexation to a transition metal, with both phosphorus lone pairs pointing toward each other. This is reflected in the high value of the ^4J(P−P) coupling constant, 58 Hz, thus suggesting a similar time-averaged conformation in solution.

To evaluate the conformational changes brought about by complexation to a metal, complex [(***anti*-(*R,S*p)-6a**)Rh(NBD)]BF$_4$ (**7a**) was prepared by reaction of equivalent amounts of [Rh(NBD)$_2$]BF$_4$ and ***anti*-(*R,S*p)-6a** in methylene chloride. Attempts to obtain crystals suitable for X-ray determination, however, failed and the complex was characterized solely by nuclear magnetic resonance. To compare their spectroscopic properties, the complexes [(***anti*-(*R,S*p)-6b**)Rh(NBD)]BF$_4$ (**7b**) and [(***anti*-(*S,R*p)-6c**)Rh(NBD)]BF$_4$ (**7c**) were prepared as well by mixing 1 equiv of [Rh(NBD)$_2$]BF$_4$ and 1.1 equiv of ***anti*-(*R,S*p)-6b** and ***anti*-(*S,R*p)-6c**, respectively, in deuterated acetone. The ^{1}H and ^{31}P NMR spectra were recorded after stirring the solutions for 2 h (Table 4). Only the expected complexes and free norbornadiene could be detected.

Upon coordination to Rh, ^{31}P NMR chemical shifts move downfield.[29] The coordination shift ($\Delta = \delta_{\text{complex}} - \delta_{\text{free ligand}}$) for the diphenylphosphino group is larger than that for the dialkylphosphino group in the same compound, indicating a greater change in the *SPS* angle (*S* = substituent on phosphorus) upon coordination for the former group. The observed downfield shift is less for the bulkier P-*t*-Bu$_2$ group than for the PPh$_2$ and PCy$_2$ groups: this is because *SPS* angles of ligands with larger substituents generally open less on coordination.

Table 4. ^{31}P NMR[a] Data of [(P*P)Rh(NBD)]BF_4 Complexes

		$\delta(^{31}P)$ (ppm)		J (Hz)			Δ (δ(complex) − δ(lig))	
complex	R	*o*-PPh_2	α-PR_2	P−P	*o*-P−Rh	αP−Rh	Δ(*o*-PPh_2)	Δ(α-PR_2)
[(***R*,*Sp*)-6a**]Rh(NBD)]BF_4	Ph	34.50	55.86	40.3	155.7	157.5	50.52	49.30
[(***S*,*Rp*)-6c**]Rh(NBD)]BF_4[b]	Cy	33.33	53.52	38.1	158.5	151.2	52.13	36.81
[(***R*,*Sp*)-6b**]Rh(NBD)]BF_4[b]	*t*-Bu	35.06	74.28	37.7	160.1	147.6	54.19	24.23

[a] Spectra recorded in CD_3COCD_3. [b] The complexes were prepared in situ.

Scheme 4. Hydrogenation of Methyl (*Z*)-*N*-Acetamidocinnamate

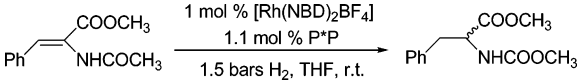

Table 5. Results of Hydrogenation of Methyl (*Z*)-*N*-Acetamidocinnamate with [(P*P)Rh(NBD)]BF_4[a]

P*P	α-PR_2	time (h)	yield[b] (%)	ee[b] (%)
(*R*,*Sp*)-6a	Ph	18	100	22 (*S*)
(*R*,*Sp*)-6b	*t*-Bu	18	100	9 (*S*)
(*S*,*Rp*)-6c	Cy	1	100	88 (*S*)

[a] The catalyst precursors were generated in situ. [b] Determined by GC; see Experimental Section for details.

Hydrogenation of Prochiral Olefins. The effectiveness of the new [(η^6-arene)Cr($CO)_3$]-based diphosphines in asymmetric catalysis was tested in the Rh-promoted hydrogenation of methyl (*Z*)-*N*-acetylaminocinnamate and dimethyl itaconate.[33] The catalyst precursor [Rh(P*P)(NBD)]BF_4 was more conveniently prepared in situ by mixing [$Rh(NBD)_2$]BF_4 and the ligand in the solvent in which the reaction was to be carried out. A 10% phosphine excess was used to compensate for partial ligand oxidation by traces of air in the hydrogenation system. Furthermore, this ensures that all the metal atoms present will be coordinated, avoiding an achiral reaction channel which would be open if the metal component were in excess. The solution was stirred for 15 min before being added to a solution of the substrate in the same solvent.

The active catalyst [Rh(P*P)sol_2]BF_4 is generated by removal of the diolefin via hydrogenation. It has been recently reported that hydrogenation of COD takes considerably longer that of than NBD.[34] At a substrate to catalyst molar ratio of 100, a significant amount of the expensive COD precatalyst is unreacted at the end of the reaction: that is, it is unavailable for the intended asymmetric hydrogenation, because it is blocked by the diolefin. Because this has been shown to be the case also for diolefin Rh complexes containing [(η^6-arene)Cr($CO)_3$]-based diphosphines,[13] the faster reacting NBD diolefin was preferred to prepare the catalyst precursor. Hydrogenation of methyl (*Z*)-*N*-acetamidocinnamate was carried out using a substrate-to-catalyst ratio of 100, in THF at room temperature, under an initial pressure of 1,5 bar (Scheme 4, Table 5).

The substrate concentration was 0.05 M: in fact, high optical yields are usually obtained at low substrate concentration, probably because at higher substrate concentrations a 2:1 ratio of substrate to Rh complex is formed in addition to the expected 1:1 complex.[1b] Results of hydrogenation under these conditions are reported in Table 5. Among the three ligands, the one bearing a PCy_2 group in the benzylic position provides a catalyst precursor, which performs much better in terms of both activity and enantioselectivity. Assuming that the Halpern mechanism holds good for this catalytic system[35]—the so-called "unsaturated mechanism" in which hydrogenation occurs after binding of the substrate to the catalyst—the increased reactivity and enantioselectivity might be related to the enhanced electron density at rhodium brought about by this electron-rich diphosphine.[36,37] Oxidative addition of H_2 to rhodium is the rate-determining step, and the better enantioselectivity presumably arises from the higher difference in the relative rates of H_2 oxidative addition to one of the possible diastereomer complexes, [(P*P)Rh^I(substrate)], induced by the PCy_2 ligand compared to the other ligands. The ligand electronic and/or steric properties might have effects also on the metal center ability to bind π-ligands and consequently on the intrinsic stabilities (and thus relative concentrations) and reactivities of the four diastereomeric [(P*P)Rh^I(substrate)] adducts which are possible for a C_1-symmetric ligand (Chart 2).[38]

Gridnev and Imamomto have recently investigated the mechanism of asymmetric hydrogenation catalyzed by a rhodium complex of (*S*,*S*)-1,2-bis(*tert*-butylmethylphosphino)ethane, an electron-rich diphosphine, and have shown that the electron-donating substituents in the ligand increase the affinity of its rhodium(I) solvate complex toward dihydrogen.[33] They have been able to observe a Rh dihydride complex with a diphosphine ligand, and this, together with experimental data they have collected, requires that a dihydride mechanism—

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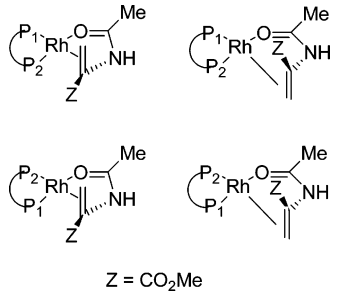
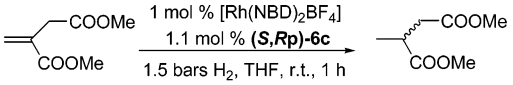
Chart 2. Diastereomeric [(P*P)Rh(olefin)]BF_4 Complexes for a C_1-Symmetric Diphosphine



Scheme 5. Hydrogenation of Dimethyl Itaconate



100 % y. 87 % e.e. (*R*)

in which oxidative addition of hydrogen to the catalyst precedes the coordination of the substrate—is operating in the case of asymmetric hydrogenation catalyzed by Rh complexes of electron-rich diphosphines. This alternative mechanism then has to be considered for hydrogenation catalyzed by a rhodium catalyst supported by the ligand **(*S*,*R*p)-6c**. However, Brown et al., by detecting agostic intermediates in the asymmetric hydrogenation of dehydroamino acids catalyzed by Rh−PHANEPHOS complex, have proven the reversibility of all stages of hydrogenation that precede the migratory insertion of the coordinated olefin into the Rh−H bond.[39] Migratory insertion is then the irreversible stereodetermining step. If an equilibrium exists among substrate, $[(P^*P)Rh^I(solvent)_2]$, and $[(P^*P)Rh^{III}(H)_2]$, then which of the two alternative reaction pathways (unsaturated and dihydride) is operative in hydrogenation is not primarily important for stereoselection, because on all previous stages the intermediates providing different stereoselection are in equilibrium and the two mechanisms then lead to a common pathway before formation of the Rh−monohydride−alkyl intermediate, when stereoselection actually occurs.

When PCy_2 is replaced by a P-*t*-Bu_2 or a PPh_2 donor group in the benzylic site of the ligand, a marked drop in the enantioselectivity of hydrogenation is observed. The steric demands of the other substituents at phosphorus probably do not provide the high asymmetry of the enviroment around rhodium brought about by the PPh_2/PCy_2 donor combination, and this smoothes the difference in reactivity among intermediates leading to opposite enantiomers of the hydrogenated product.

Only the best-performing ligand was tested in the hydrogenation of dimethyl itaconate under identical reaction conditions: the reaction was stopped after 1 h and complete conversion to dimethyl 2-succinate was observed (Scheme 5). The enantioselectivity was 87% ee.

The new ligands, in which the phosphorus donor groups are supported by the Indane framework, provide catalytic results which are comparable with those of the parent Daniphos ligands: in the hydrogenation of methyl (*Z*)-*N*-acetamidocinnamate, the ligand **(*S*,*R*p)-6c** brings about a slighthly higher ee compared to the analogous **(*R*,*S*p)-1c**[13] under similar experimental conditions (88% vs 81.5% ee). For the bis(diphenylphosphino) ligand, the presence of a more conformationally constrained backbone induces a more significant improvement in selectivity: 22% ee with the ligand **(*R*,*S*p)-6a** vs 10.3% ee achieved with the **(*R*,*S*p)-1a** ligand. In the hydrogenation of dimethyl itaconate, the ligand **(*S*,*R*p)-6c** induces 87% ee while the ligand **(*R*,*S*p)-1c** only provides 70% ee.

Conclusion

Although outstanding ligands exist for the enantioselective hydrogenation of prochiral olefins,[12a] the demand for new ligands arises from the observation that no class of ligands can be considered universal, as it is generally linked to a finite, however, broad scope of substrates and reactions. In addition, successful ligands are usually protected by patents.

As part of our program to extend the diversity of chiral diphosphines based on $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes, three new ligands have been prepared, starting from easily availabe, optically pure (*S*)-(1-dimethylamino)indane. By proper choice of reaction conditions, complexation of this amine to the $Cr(CO)_3$ moiety turns out to be highly diastereoselective. The originally designed synthetic strategy[6,10] is then smoothly applied to the synthesis of diphosphines supported on the more rigid scaffold provided by the indane framework. In the enantioselective hydrogenation of methyl (*Z*)-*N*-acetamidocinnamate and dimethyl itaconate promoted by rhodium complexes, catalytic performances are dependent on the electron richness and steric demand of the phosphorus substituents, although no correlation can be drawn. In comparison to the parent Daniphos ligands, some improvement as to enantioselectivity is observed.[13]

Prompted by the positive results obtained in asymmetric hydrogenation, further applications of these ligands in homogeneous catalysis are in progress.

Experimental Section

Materials and Methods. All reactions, involving air- and moisture-sensitive compounds, and subsequent workup were carried out under nitrogen using Schlenk and syringe techniques. Reactions were monitored by analytical thin-layer chromatography (TLC) using either Merck silica gel 60 F_{254} or Merck aluminum oxide F_{254} aluminum cards. The chromatograms were visualized with UV light. Solutions of crude reaction mixtures were filtered through a short bed of filter aid Fluka Celite 535. The solvent was evaporated. Flash chromatography of the crude products was performed either on silica gel 60 (Merck, particle size 0.063−0.200, pH 7.0 ± 0.5) or aluminum oxide 90 II-III (Merck, particle size 0.063−0.200, pH 9.0 ± 0.5). Solvents were dried and deoxygenated by standard procedures. NMR spectra were recorded on a Varian Mercury 200 spectrometer operating at 200 MHz (for ^1H), 50 MHz (for ^{13}C), and 81 MHz (for ^{31}P), on a Varian Mercury Plus spectrometer operating at 400 MHz (for ^1H) and 182 MHz (for ^{13}C), and on a Varian Unity 500 spectrometer operating at 500 MHz (for ^1H), 125 MHz (for ^{13}C), and 202 MHz (for ^{31}P) at ambient temperature. Chemical shifts (δ) are given in ppm relative to TMS (^1H, ^{13}C) and 85% H_3PO_4 as external standards (^{31}P). IR spectra were recorded on a Perkin-

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Elmer FT-IR Model 1720-X spectrometer. Optical rotations were measured in 1 dm cells on a Perkin-Elmer Model 341 polarimeter at ambient temperature. Mass spectra were obtained by electron impact (EI) or chemical ionization (CI) with isobutane on a Finnigan MAT 95 spectrometer. Elemental analyses were obtained on a Carlo Erba Strumentazione Element Analyzer. Model 1106. A generous loan of (*S*)-1-aminoindane was kindly provided by BASF GmbH. The following substances were prepared according to published procedures: $[Rh(NBD)Cl]_2$,[40] $[Rh(NBD)_2]BF_4$,[41] [(η^6-naphthalene)$Cr(CO)_3$].[19] All other chemicals were purchased and used without further purification.

X-ray Single-Crystal Analysis. Suitable crystals of ***syn*-(*S*,*S*p)-4** and **(*S*,*R*p)-6a·**(benzene) were mounted on glass fibers. Geometry and intensity data were collected using an ENRAF-Nonius CAD4 diffractometer.[42] Lattice parameters and orientation matrixes were obtained from 25 centered reflections. All data were collected using graphite-monochromated Mo Kα radiation (wavelength 0.710 73 Å) with the $\omega/2\theta$ scan method. Data were processed using the MolEN program.[43] Empirical absorption corrections were applied by ψ scans. The structures were solved by direct methods and refined using SHELXTL.[44] Non-hydrogen atoms were refined with anisotropic displacement parameters, except that the cocrystallized solvent benzene in **(*S*,*R*p)-6a·**(benzene) was treated as a rigid hexagon. Hydrogen atoms were placed in idealized positions (C−H = 0.98 Å) and included as riding with $U_{iso}(H) = 1.3$-[U_{eq}(non-H)]. Displacement ellipsoid plots were drawn with the help of the PLATON program.[45] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-237549 (***syn*-(*S*,*S*p)-4**) and CCDC-237548 (**(*S*,*R*p)-6a·**(benzene)). Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ U.K. (fax, +44-(0)1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

Hydrogenation Reactions. Hydrogenation reactions were run in a Buchi Miniclave 250 mL glass reactor. The sequence N_2−vacuum was applied three times. The inert gas was then replaced with H_2. Reactions were performed in THF. The substrate (1 mmol) was weighed in a Schlenk flask. The flask was then purged with nitrogen, and 5 mL of the dry solvent was added. After complete substrate solubilization, the solution was transferred into the autoclave by means of a syringe while a stream of hydrogen was allowed to flow through the autoclave inlet. A 5 mL portion of the solvent was used to wash the Schlenk flask and transferred into the autoclave. The solution was vigorously stirred with a magnetic bar using a hot plate magnetic stirrer. {$[Rh(nbd)_2]BF_4$} (0.01 mmol) and the ligand (0.011 mmol) were placed in a Schlenk flask under nitrogen, and 5 mL of the same solvent used to solubilize the substrate was added. The solution was stirred for 15 min before being transferred into the autoclave. The flask was rinsed with 5 mL of solvent, and this solvent was also injected into the autoclave. The hydrogen pressure was then set to the required value.

substrate	1 mmol	[substrate] = 0.05 M
{$[Rh(nbd)_2]BF_4$}	0.01 mmol	[substrate]/[Rh] = 100
ligand	0.011 mmol	[ligand]/[Rh] = 1.1

At the end of the reaction, the autoclave was vented and the crude reaction mixture filtered through a short pad of Celite to get rid of the metal catalyst. The sample was then checked for conversion and enantiomeric excess by means of GC-MS and GC. *N*-Acetylfenylalanine methyl ester: achiral column; AT-5 (30 m, i.d. 0.25 mm, ft 0.25 μm); temperature 80 °C, 1 min, 15 °C/min; 280 °C; injector 280 °C; detector 280 °C; carrier helium, 16.9 psi; R_t(*N*-acetylphenylalanine methyl ester) = 6.75 min. R_t(methyl (*Z*)-*N*-acetamidocinnamate) = 7.82 min. Chiral: column Chirasil-Val-L (50 m, i.d. 0.32 mm, ft 0.25 μm); temperature 110 °C, 5 min, 1.5 °C/min; 180 °C, 1 min, 2 °C/min; 200 °C, 30 min; injector PTV; detector 250 °C; carrier nitrogen, 20 psi; $R_t(R)$ = 48.4 min, $R_t(S)$ = 49.6 min. 2-Methylsuccinic acid dimethyl ester: achiral column AT-5 (30 m, i.d. 0.25 mm, ft 0.25 μm); temperature 80 °C, 1 min, 15 °C/min; 280 °C; injector 280 °C; detector 280 °C; carrier helium, 16.9 psi; R_t(2-methylsuccinic acid dimethyl ester) = 8.85 min, R_t(dimethyl itaconate) = 9.17. Chiral: column Lipodex E; temperature 80 °C, 5 min, 10 °C/min; 120 °C, 5 min, 10 °C/min; 170 °C, 15 min; injector 220 °C; detector 250 °C; $R_t(S)$ = 7.59 min, $R_t(R)$ = 7.67 min.

(*S*)-1-Aminoindane ((*S*)-2). (*S*)-1-Aminoindane was methylated according to the Eschweiler−Clarke procedure with formic acid and formaldehyde.[15] Formaldehyde (37% aqueous solution, d 1.090, 50.8 mL, 3 equiv) followed by formic acid (98% aqueous solution, d 1.220, 42.5 mL, 5 equiv) were added dropwise to the amine (30 g, 0.22 mol, 1 equiv) at 0 °C. The solution was heated at 80 °C overnight and then cooled and acidified with 10 N HCl. The aqueous solution was extracted with diethyl ether and then basified with 50% aqueous NaOH. The basic aqueous phase was extracted three times with diethyl ether; the combined ether extracts were washed with water and then dried over $MgSO_4$. Diethyl ether was evaporated and the crude product distilled under reduced pressure to give the protected amine **(*S*)-2** as a colorless oil (23.2 g, 0.14 mol, 64%). ^{1}H NMR (500 MHz, C_6D_6): δ 1.71 (dddd, 1 H, $J_{HH,gem}$ = 12.4 Hz, $J_{HH,cis}$ = 8.7 Hz, $J_{HH,cis}$ = 7.7 Hz, $J_{HH,trans}$ = 4.7 Hz, *H*2as), 1.86 (ddt, 1 H, $J_{HH,gem}$ = 13.0 Hz, $J_{HH,cis}$ = 8.7 Hz, $J_{HH,trans}$ = 6.7 Hz, *H*2eq), 2.12 (s, 6 H, $N(CH_3)_2$), 2.29 (ddd, 1 H, $J_{HH,gem}$ = 15.8 Hz, $J_{HH,cis}$ = 9.1 Hz, $J_{HH,trans}$ = 4.7 Hz, *H*3as), 2.73 (ddd, 1 H, $J_{HH,gem}$ = 15.8 Hz, $J_{HH,cis}$ = 8.4 Hz, $J_{HH,trans}$ = 7.4 Hz, *H*3eq), 4.20 (t, 1 H, *J* = 7.0 Hz, *H*1), 7.09−7.17 (m, 3 H, H_{AR}), 7.50 (m, 1 H, H_{AR}). ^{13}C NMR (125 MHz, C_6D_6): δ 23.06 (*C*2), 30.96 (*C*3), 40.86 (*C*10), 70.37 (*C*1), 124.77 (CH_{AR}), 125.68 (CH_{AR}), 126.52 (CH_{AR}), 127.63 (CH_{AR}), 143.82 (C_{AR}), 144.23 (C_{AR}). MS (EI; *m*/*z*): 161 (M^+, 70%), 160 (M − H, 100%), 117 (M − $N(CH_3)_2$, 97%). Bp (10 Torr): 99−100 °C. $[\alpha]_D^{RT} = -72.1°$ (neat).

***syn*-(*S*,*S*p)-[η^6-1-(dimethylamino)indane]$Cr(CO)_3$ (*syn*-(*S*,*S*p)-3) and *anti*-(*S*,*R*p)-[η^6-1-(dimethylamino)indane]-$Cr(CO)_3$ (*anti*-(*S*,*R*p)-3). (a) Thermolysis with $Cr(CO)_6$ (Table 1, Entry 1).** A mixture of (*S*)-2 (15.0 g, 93.0 mmol) and $Cr(CO)_6$ (24.6 g, 112.0 mmol) in di-*n*-butyl ether (296 mL) and THF (37 mL) was heated under reflux (bath temperature 140 °C) for 66 h (Table 1, entry 1). The solution was cooled and filtered through a short pad of Celite on a sintered-glass filter. The solvents were distilled at reduced pressure (an oil pump was required to remove the solvents and uncomplexed amine completely). ***syn*-(*S*,*S*p)-3** and ***anti*-(*S*,*R*p)-3** were collected as a single fraction after column chromatography (aluminum oxide, hexane/ethyl acetate 4/1). ^{1}H NMR indicated a 42/58 ratio of ***syn*-(*S*,*S*p)-3** and ***anti*-(*S*,*R*p)-3**. Further attempts at quantitatively separating the two diastereoisomers by column chromatography failed. Fractional crystallization from dichloromethane/hexane at −30 °C gave yellow crystals of the syn and anti isomers in a 17/83 ratio. Yield (after coulmn chromatography): 9.68 g (35%). R_f = 0.42 (aluminum oxide, hexane/ethyl acetate 4/1).

(b) Arene Exchange with [(η^6-naphthalene)$Cr(CO)_3$]. Synthesis A (Table 1, Entries 2−4). A mixture of [(η^6-naphthalene)$Cr(CO)_3$] (0.53 g, 2.0 mmol) and **(*S*)-2** (0.48 g, 3.0

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mmol) in the reported solvent (10 mL) was heated in the dark under the conditions reported in Table 1, entries 2−4. Volatiles were removed under reduced pressure, the residue was dissolved in diethyl ether, and the solution was filtered through a short pad of Celite on a sintered-glass filter. The ratio of the syn and anti isomers was determined from the ^{1}H NMR spectrum of the crude product. The crude product was purified by column chromatography (silica gel, diethyl ether).

Synthesis B (Table 1, Entry 5). A mixture of [(η^6-naphthalene)Cr(CO)$_3$] (2.56 g, 9.7 mmol) **(*S*)-2** (1.30 g, 8.1 mmol), and tetrahydrofuran (0.87 g, 12.1 mmol) in di-*n*-butyl ether (50 mL) was heated at 75 °C (temperature of the oil bath) for 91 h in the dark. Volatiles were removed under reduced pressure, the residue was dissolved in diethyl ether, and the solution was filtered through a short pad of Celite on a sintered-glass filter. The ^{1}H NMR spectrum of the crude product showed a 94/6 ratio of the syn and anti diastereoisomers. After elution of an orange-red band (mixture of naphthalene and unreacted [(naphthalene)Cr(CO)$_3$]) with diethyl ether, pure yellow ***syn*-(*S*,*S*p)-3** was eluted using acetone.Yield: 2.19 g (91%) of pure ***syn*-(*S*,*S*p)-3**.

***syn*-(*S*,*S*p)-3.** ^{1}H NMR (500 MHz, C_6D_6): δ 1.38 (m, 1 H, J = 11.9 Hz, J = 7.0 Hz, *H*2), 1.82 (m, 1 H, *H*2), 1.97 (ddd, 1 H, J = 15.5 Hz, J = 7.3 Hz, *H*3), 2.22 (ddd, 1 H, J = 15.5 Hz, J = 8.2 Hz, *H*3), 2.26 (s, 6 H, *H*10), 3.47 (dd, 1 H, J = 11.0 Hz, J = 7.0 Hz, *H*1), 4.18 (t, 1 H, J = 6.1 Hz, *H*6), 4.33 (d, 1 H, J = 6.1 Hz, *H*4), 4.68 (t, 1 H, J = 6.1 Hz, *H*5), 5.30 (d, J = 6.1 Hz, *H*7). ^{13}C NMR (125 MHz, C_6D_6): δ 21.17 (*C*2), 28.22 (*C*3), 41.40 (*C*10), 67.97 (*C*1), 85.90 (*C*4), 86.99 (*C*6), 92.01 (*C*7), 95.68 (*C*5), 114.22 (C_{AR}), 115.04 (C_{AR}), 234.11 (*C*O). MS (CI, isobutane; *m*/*z*): 298 (M + H, 69%), 253 (M − N(CH$_3$)$_2$, 100%), 241 (M − 2CO, 31%), 213 (M − 3CO, 6%). IR ($CHCl_3$): ν_{CO} 1964, 1898 cm^{-1}. Anal. Calcd for $C_{14}H_{15}CrNO_3$: H, 5.09; C, 56.56; N, 4.71. Found: H, 5.27; C, 56.45; N, 4.84. $[\alpha]_D^{RT}$ = +45.9° (*c* 0.22 in $CHCl_3$).

***anti*-(*S*,*R*p)-3.** ^{1}H NMR (500 MHz, C_6D_6): δ 1.60 (m, 1 H, *H*2), 1.72 (m, 1 H, *H*2), 1.82 (s, 6 H, *H*10), 2.19−2.31 (m, 2 H, *H*3), 3.72 (d, 1 H, J = 7.6 Hz, *H*1), 4.33 (t, 1 H, J = 6.1 Hz, *H*6), 4.47 (t, 1 H, J = 6.1 Hz, *H*5), 4.58 (d, 1 H, J = 6.4 Hz, *H*4), 5.11 (d, J = 6.4 Hz, *H*7). ^{13}C NMR (125 MHz, C_6D_6): δ 23.22 (*C*2), 31.18 (*C*3), 40.96 (*C*10), 68.93 (*C*1), 89.13 (*C*4), 90.79 (*C*6), 92.35 (*C*7), 93.17 (*C*5), 111.75 (C_{AR}), 115.38 (C_{AR}), 233.66 (*C*O).

***syn*-[η^6-(*S*,*S*p)-1-(dimethylamino)-7-(diphenylphosphino)indane]Cr(CO)$_3$ (*syn*-(*S*,*S*p)-4).** ***syn*-(*S*,*S*p)-3** (2.30 g, 7.7 mmol) was dissolved in dry diethyl ether (154 mL). The solution was cooled to −78 °C, and *tert*-butyllithium (1.7 M in pentane, 5.0 mL, 8.5 mmol) was added dropwise with a syringe. After 1.5 h, chlorodiphenylphosphine (1.88 g, 8.5 mmol) was added dropwise. The reaction mixture was warmed slowly to room temperature overnight and then filtered through a short pad of Celite on a sintered-glass funnel. The solvent was distilled off on a rotary evaporator, and the crude product was purified by column chromatography (silica gel, hexane/diethyl ether 4/1 → neat diethyl ether). Yield: 3.35 g (90%). R_f = 0.33 (silica gel, hexane/diethyl ether 4/1). Crystals suitable for X-ray structure determination were grown from a mixture of acetone and hexane at −30 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 1.26 (m, 1 H, CH$_2$C*H*$_2$CH(N(CH$_3$)$_2$)), 1.87−2.01 (m, 2 H, CH$_2$C*H*$_2$CH(N(CH$_3$)$_2$), C*H*$_2$CH$_2$CH(N(CH$_3$)$_2$)), 2.04 (s, 6 H, N(C*H*$_3$)$_2$), 2.27 (m, 1 H, C*H*$_2$CH$_2$CH(N(CH$_3$)$_2$)), 3.36 (dd, 1 H, J = 11 Hz, J = 6.7 Hz, C*H*N(CH$_3$)$_2$), 4.24 (d, 1 H, J = 6.4 Hz, C*H*$_{AR}$), 4.25 (d, 1 H, J = 6.4 Hz, C*H*$_{AR}$), 4.60 (tm, 1 H, J = 6.4 Hz, C*H*$_{AR}$), 7.02 (tm, 1 H, J = 7.3 Hz, C*H* *m*,*p*-Ar$_2$P), 7.07 (tm, 5 H, J = 6.7 Hz, C*H* *m*,*p*-Ar$_2$P), 6.71 (tm, 2 H, J = 7.9 Hz, C*H* *o*-Ar$_2$P), 7.6 (t, 2 H, J = 6.7 Hz, C*H* *o*-Ar$_2$P). ^{13}C NMR (125 MHz, C_6D_6): δ 19.53 (CH$_2$*C*H$_2$CH(N(CH$_3$)$_2$)), 28.50 (*C*H$_2$CH$_2$-CH(N(CH$_3$)$_2$)), 40.39 (bs, N(*C*H$_3$)$_2$), 68.57 (d, $^3J_{CP}$ = 2.2 Hz, CH$_2$-CH$_2$*C*H(N(CH$_3$)$_2$)), 84.96 (*C*H$_{AR}$), 89.32 (d, $^2J_{CP}$ = 1.7 Hz, *C*H$_{AR}$), 95.64 (*C*H$_{AR}$), 108.64 (d, $^2J_{CP}$ = 31.2 Hz, C_{AR}), 114.81 (d, $^3J_{CP}$ = 2.7 Hz, C_{AR}), 115.55 (d, $^1J_{CP}$ = 11.5 Hz, C_{AR}), 128.57 (d, $^3J_{CP}$ = 7.6 Hz, *C*H *m*-Ar$_2$P), 129.04 (d, $^3J_{CP}$ = 6.0 Hz, *C*H *m*-Ar$_2$P), 129.41 (*C*H *p*-Ar$_2$P), 133.42 (d, $^2J_{CP}$ = 21.9 Hz, *C*H *o*-Ar$_2$P), 135.59 (d, $^2J_{CP}$ = 22.0 Hz, *C*H *o*-Ar$_2$P), 136.61 (d, $^1J_{CP}$ = 21.9 Hz, *C ipso*-Ar$_2$P), 137.23 (d, $^2J_{CP}$ = 8.2 Hz, *C ipso*-Ar$_2$P), 234.08 (d, J_{CP} = 3.3 Hz, *C*O). ^{31}P NMR (81 MHz, C_6D_6): δ −12.10. MS (CI, isobutane; *m*/*z*): 482 (M + H, 29%), 437 (M − N(CH$_3$)$_2$, 86%), 397 (M − 3CO, 37%), 346 (M + H − Cr(CO)$_3$, 100%). IR ($CHCl_3$): ν_{CO} 1960, 1888 cm^{-1}. Anal. Calcd for $C_{26}H_{24}CrNO_3P$: H, 5.02; C, 64.86; N, 2.91. Found: H, 5.18; C, 65.20; N, 3.21. $[\alpha]_D^{RT}$ = −238.0° (*c* 0.20 in $CHCl_3$).

***anti*-[η^6-(*S*,*R*p)-1-(dimethylamino)-7-(diphenylphosphino)indane]Cr(CO)$_3$ (*anti*-(*S*,*R*p)-4).** A 1:1 mixture of ***syn*-(S,Sp)-3** and ***anti*-(S,Rp)-3** (2.0 g, 6.7 mmol) was dissolved in dry diethyl ether (134 mL). The solution was cooled to −78 °C, and *tert*-butyllithium (1.7 M in pentane, 4.7 mL, 8.1 mmol) was added dropwise with a syringe. After 1.5 h, chlorodiphenylphosphine (1.78 g, 8.1 mmol) was added dropwise. The reaction mixture was warmed slowly to room temperature overnight and then filtered through a short pad of Celite on a sintered-glass funnel. The solvent was distilled off on a rotary evaporator. The ^{1}H NMR spectrum of the crude product showed a 1:1 ratio of ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-4**. The crude product was purified by column chromatography (aluminum oxide, neat hexane → hexane/diethyl ether 4/1): two fractions were collected, the first one consisting of pure ***anti*-(*S*,*R*p)-4** (1.1 g, 37% yield), R_f = 0.49 (aluminum oxide, hexane/diethyl ether 4/1), and a second fraction containing both ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-4** (1.7 g, 52% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 1.46 (s, 6 H, N(C*H*$_3$)$_2$), 1.49−1.55 (m, 2 H, CH$_2$C*H*$_2$CH(N(CH$_3$)$_2$)), 2.16 (m, 1 H, C*H*$_2$CH$_2$CH(N(CH$_3$)$_2$)), 2.30 (m, 1 H, C*H*$_2$CH$_2$CH(N(CH$_3$)$_2$)), 4.30 (t, J = 5.8 Hz, C*H*$_{AR}$), 4.61 (m, 1 H, C*H*N(CH$_3$)$_2$), 4.65 (d, J = 5.9 Hz, C*H*$_{AR}$), 4.74 (d, J = 5.5 Hz, C*H*$_{AR}$), 7.06 (m, 4 H, C*H* *m*,*p*-Ar$_2$P), 7.14 (m, 2 H, C*H* *m*,*p*-Ar$_2$P), 7.29 (tm, 2 H, J = 7 Hz, C*H* *o*-Ar$_2$P), 7.61 (tm, 2 H, J = 7 Hz, C*H* *o*-Ar$_2$P). ^{13}C NMR (125 MHz, C_6D_6): δ 19.29 (CH$_2$*C*H$_2$CH(N(CH$_3$)$_2$)), 32.00 (*C*H$_2$CH$_2$CH(N(CH$_3$)$_2$)), 39.13 (N(*C*H$_3$)$_2$), 68.35 (d, $^3J_{CP}$ = 8.3 Hz, CH$_2$CH$_2$*C*H(N(CH$_3$)$_2$)), 90.67 (d, $^3J_{CP}$ = 1.7 Hz, *C*H$_{AR}$), 91.36 (*C*H$_{AR}$), 97.35 (d, $^2J_{CP}$ = 4.3 Hz, *C*H$_{AR}$), 103.84 (d, $^2J_{CP}$ = 26.9 Hz, C_{AR}), 111.86 (d, $^3J_{CP}$ = 4.9 Hz, C_{AR}), 117.73 (d, $^1J_{CP}$ = 23.1 Hz, C_{AR}), 128.10 (d, $^3J_{CP}$ = 13.1 Hz, *C*H *m*-Ar$_2$P), 128.75 (d, $^3J_{CP}$ = 6.6 Hz, *C*H *m*-Ar$_2$P), 129.31 (*C*H *p*-Ar$_2$P), 133.35 (d, $^2J_{CP}$ = 21.4 Hz, *C*H *o*-Ar$_2$P), 134.62 (d, $^2J_{CP}$ = 19.1 Hz, *C*H *o*-Ar$_2$P), 135.81 (d, $^1J_{CP}$ = 13.2 Hz, *C ipso*-Ar$_2$P), 138.06 (d, $^1J_{CP}$ = 8.8 Hz, *C ipso*-Ar$_2$P), 233.22 (*C*O). ^{31}P NMR (81 MHz, C_6D_6): δ −15.20. MS (EI; *m*/*z*): 481 (M$^+$, 25%), 437 (M − N(CH$_3$)$_2$, 37%), 425 (M − 2CO, 69%), 397 (M − 3CO, 100%), 345 (M − Cr(CO)$_3$, 19%). IR ($CHCl_3$): ν_{CO} 1965, 1895 cm^{-1}. Anal. Calcd for $C_{26}H_{24}CrNO_3P$: H, 5.02; C, 64.86; N, 2.91. Found: H, 5.66; C, 66.22; N, 3.16. $[\alpha]_D^{RT}$ = +288.6° (*c* 0.07 in $CHCl_3$).

***anti*-[η^6-(*R*,*S*p)-1-chloro-7-(diphenylphosphino)indane]-Cr(CO)$_3$ (*anti*-(*R*,*S*p)-5).** ***syn*-(*S*,*S*p)-4** (1.37 g, 2.8 mmol) was dissolved in dry tetrahydrofuran (56 mL). The solution was cooled to −40 °C, and 1-chloroethyl chloroformate (1.24 mL, 11.3 mmol, d 1.312) was added dropwise. The reaction mixture was warmed to room temperature and stirred until complete conversion. The course of the reaction was monitored by ^{31}P NMR on a small sample of the crude reaction mixture dissolved in C_6D_6. The solvent and the byproduct (CH$_3$)$_2$NC(O)CHClCH$_3$ were distilled off. The residue was redissolved in diethyl ether and the solution filtered through a short pad of Celite on a sintered-glass funnel. Evaporation of the solvent gave a yellow solid (1.4 g) which, on the basis of ^{1}H, ^{13}C, and ^{31}P NMR, could be reasonably identified as mainly ***anti*-(*R*,*S*p)-5** (disappearance of the signal due to N*Me*$_2$). Attempts at purification by means of column chromatography and/or crystallization failed, due to easy deterioration. The crude product was used as such for the preparation of the diphosphine ligands. ^{1}H NMR (500 MHz, C_6D_6): δ 1.67 (m, 1 H, C*H*$_2$CH$_2$CH(N(CH$_3$)$_2$)), 1.95−2.05 (ms, 2 H, CH$_2$C*H*$_2$CH(N(CH$_3$)$_2$, C*H*$_2$CH$_2$CH(N(CH$_3$)$_2$)), 2.49 (m, 1 H, CH$_2$C*H*$_2$CH(N(CH$_3$)$_2$)), 4.20 (t, 1 H, J = 6.4 Hz, C*H*$_{AR}$),

4.57 (d, 1 H, J = 5.5 Hz, CH_{AR}), 4.62 (d, 1 H, J = 6.4 Hz, CH_{AR}), 5.58 (dd, 1 H, J = 5.2 Hz, J = 1.8 Hz, CH(N(CH$_3$)$_2$)), 7.03−7.13 (ms, 6 H, CH *m,p*-Ar$_2$P), 7.37 (tm, J = 7.3 Hz, CH *o*-Ar$_2$P), 7.56 (tm, J = 7.3 CH *o*-Ar$_2$P). ^{13}C NMR (125 MHz, C_6D_6): δ 28.66 (CH$_2$*C*H$_2$CH(N(CH$_3$)$_2$)), 35.25 (*C*H$_2$CH$_2$CH(N(CH$_3$)$_2$)), 62.12 (d, $^3J_{CP}$ = 13.1 Hz, *C*HCl), 90.90 (*C*H$_{AR}$), 91.83 (*C*H$_{AR}$), 96.81 (*C*H$_{AR}$), 100.83 (d, $^1J_{CP}$ = 26.3 Hz, *C*$_{AR}$), 110.78 (d, $^3J_{CP}$ = 26.3 Hz, *C*$_{AR}$), 117.04 (d, $^2J_{CP}$ = 26.3 Hz, *C*$_{AR}$), 128.57 (d, $^3J_{CP}$ = 7.1 Hz, *C*H *m*-Ar$_2$P), 128.90 (d, $^3J_{CP}$ = 7.1 Hz, *C*H *m*-Ar$_2$P), 129.22 (*C*H *p*-Ar$_2$P), 129.87 (*C*H *p*-Ar$_2$P), 134.05 (d, $^2J_{CP}$ = 19.8 Hz, *C*H *o*-Ar$_2$P), 134.72 (d, $^2J_{CP}$ = 19.8 Hz, *C*H *o*-Ar$_2$P), 136.12 (d, $^1J_{CP}$ = 8.8 Hz, *C ipso*-Ar$_2$P), 232.24 (*C*O). ^{31}P NMR (81 MHz, C_6D_6): δ −16.33.

***anti*-[η^6-(*S,R*p)-1-chloro-7-(diphenylphosphino)indane]-Cr(CO)$_3$ (*anti*-(*S,R*p)-5).** By the same procedure used for the preparation of ***anti*-(*R,S*p)-5**, ***anti*-(*S,R*p)-5** was prepared from ***anti*-(*S,R*p)-4** (0.53 g, 1.1 mmol) and 1-chloroethyl chloroformate (0.5 mL, 4.4 mmol, d 1.312) in dry tetrahydrofuran (22 mL). The crude product (0.48 g) was used as such for the preparation of diphosphines.

***anti*-[η^6-(*R,S*p)-1,7-bis(diphenylphosphino)indane]Cr(CO)$_3$ (*anti*-(*R,S*p)-6a). *anti*-(*R,S*p)-5** (0.7 g of crude product, ∼1.5 mmol) was dissolved in dry acetone, and diphenylphosphine (0.28 g, 1.5 mmol) was added. To this solution was added very slowly dropwise a suspension of $TlPF_6$ (0.52 g, 1.5 mmol) in dry acetone (final concentration of Cr in acetone [Cr] = 0.05 M). A fine white precipitate formed immediately. The solution was stirred at room temperature overnight. NEt_3 (2.25 mL) was added, and the solution was stirred for a further 15 min and then filtered through a short pad of Celite on a sintered-glass funnel to remove TlCl. The solvent and excess NEt_3 were distilled off, and the crude product was purified by column chromatography (aluminum oxide, neat hexane → diethyl ether/hexane 1/4), followed by crystallization from dichloromethane/hexane at −30 °C. Yield: 0.70 g (79%) over two steps from ***syn*-(*S,S*p)-4** (0.68 g, 1.4 mmol). R_f = 0.42 (aluminum oxide, hexane/diethyl ether 4/1). ^{1}H NMR (500 MHz, C_6D_6): δ 0.92 (m, 1 H, CH(PPh$_2$)CH$_2$C*H*$_2$), 1.82 (bdd, 1 H, J = 15.3 Hz, J = 8.8 Hz, CH(PPh$_2$)CH$_2$C*H*$_2$), 1.98 (ddd, 1 H, J = 12.5 Hz, J = 7.9 Hz, J = 4.3 Hz, CH(PPh$_2$)C*H*$_2$CH$_2$), 2.37 (m, 1 H, CH(PPh$_2$)C*H*$_2$CH$_2$), 4.25 (t, 1 H, J = 6.4 Hz, C*H*$_{AR}$(Cr)), 4.68 (d, 1 H, J = 6.4 Hz, C*H*$_{AR}$(Cr)), 4.70 (dd, 1 H, J = 4 Hz, J = 8.8 Hz, C*H*(PPh$_2$)CH$_2$CH$_2$), 5.04 (bd, 1 H, J = 6.1 Hz, C*H*$_{AR}$(Cr)), 6.85 (tm, 2 H, J = 7.0 Hz, C*H* Ph$_2$P), 6.96 (tm, 2 H, J = 7.3 Hz, C*H* Ph$_2$P), 7.00 (m, 4 H, C*H* Ph$_2$P), 7.08 (tm, 2 H, J = 7.0 Hz, C*H* Ph$_2$P), 7.16 (m, 6 H, C*H*-Ph$_2$P), 7.58 (tm, 2 H, J = 7.0 Hz, C*H* Ph$_2$P), 7.71 (tm, 2 H, J = 7.3 Hz, C*H* Ph$_2$P). ^{13}C NMR (125 MHz, C_6D_6): δ 27.08 (CH(PPh$_2$)*C*H$_2$CH$_2$), 31.37 (CH(PPh$_2$)CH$_2$*C*H$_2$), 42.41 (dd, $^1J_{CP}$ = 22.0 Hz, $^3J_{CP}$ = 9.3 Hz, *C*H(PPh$_2$)CH$_2$CH$_2$), 89.53 (*C*H$_{AR}$(Cr)), 92.98 (*C*H$_{AR}$(Cr)), 99.20 (d, $^2J_{CP}$ = 3.3 Hz, *C*H$_{AR}$(Cr)), 100.22 (d, $^1J_{CP}$ = 28.0 Hz, *C*$_{AR}$-(Cr)), 111.12 (d, $^3J_{CP}$ = 7.1 Hz, *C*$_{AR}$(Cr)), 122.86 (dd, $^2J_{CP}$ = 26.3 Hz, $^2J_{CP}$ = 19.8 Hz, *C*$_{AR}$(Cr)), 128.57 (d, $^3J_{CP}$ = 7.1 Hz, *m*-*C*H Ph$_2$P), 128.81 (d, $^3J_{CP}$ = 7.1 Hz, *m*-*C*H Ph$_2$P), 129.30 (*p*-*C*H Ph$_2$P), 132.13 (d, $^2J_{CP}$ = 15.9 Hz, *o*-*C*H Ph$_2$P), 133.95 (dd, $^2J_{CP}$ = 19.2 Hz, J_{CP} = 2.2 Hz, *o*-*C*H Ph$_2$P), 134.22 (d, $^2J_{CP}$ = 19.7 Hz, *o*-*C*H Ph$_2$P), 135.08 (d, $^2J_{CP}$ = 20.3 Hz, *o*-*C*H Ph$_2$P), 135.98 (d, $^1J_{CP}$ = 24.7 Hz, *ipso-C* Ph$_2$P), 136.31 (d, $^2J_{CP}$ = 17.6 Hz, *ipso-C* Ph$_2$P), 136.84 (dd, $^1J_{CP}$ = 12.6 Hz, J_{CP} = 3.9 Hz, *ipso-C* 138.23 (m, *ipso-C*-Ph$_2$P), 233.20 (*C*O). ^{31}P NMR (162 MHz, C_6D_6): δ 6.56 (d, J_{PP} = 58.0 Hz, α-PPh$_2$), −16.02 (d, J_{PP} = 58.0 Hz, *o*-PPh$_2$). MS (CI, isobutane; *m/z*): 623 (M + H, 100%), 538 (M − 3CO, 43%), 346 (M + H − Cr(CO)$_3$, 19%). IR ($CHCl_3$): ν_{CO} 1962, 1897 cm^{-1}. Anal. Calcd for $C_{36}H_{28}CrO_3P_2$: H, 4.53; C, 69.45. Found: H, 4.59; C, 69.26. $[\alpha]_D^{RT}$ = −391.3° (*c* 031 in $CHCl_3$).

***anti*-[η^6-(*R,S*p)-1-(di-*tert*-butylphosphino)-7-(diphenylphosphino)indane]Cr(CO)$_3$ (*anti*-(*R,S*p)-6b). *anti*-(*R,S*p)-5** (0.7 g of crude product, ∼1.5 mmol) was dissolved in dry acetone, and di-*tert*-butylphosphine (0.22 g, 1.5 mmol) was added. To this solution was added dropwise very slowly a suspension of $TlPF_6$ (0.52 g, 1.5 mmol) in dry acetone (final concentration of Cr in acetone [Cr] = 0.05 M). A fine white precipitate formed immediately. The solution was stirred at room temperature overnight. NEt_3 (2.25 mL) was added, and the solution was stirred for a further 15 min and then filtered through a short pad of Celite on a sintered-glass funnel to remove TlCl. The solvent and excess NEt_3 were distilled off and the crude product purified by column chromatographic crystallization from dichloromethane/hexane at −30 °C. Yield: 0.30 g (37%) over two steps from ***syn*-(*S,S*p)-4** (0.68 g, 1.4 mmol). R_f = 0.53 (aluminum oxide, hexane/diethyl ether 4/1). ^{1}H NMR (500 MHz, C_6D_6): δ 0.73 (d, 9H, J = 10.1 Hz, P[C(C*H*$_3$)$_3$]$_2$), 1.21 (d, 9H, J = 9.8 Hz, P[C(C*H*$_3$)$_3$]$_2$), 2.20 (m, 2H, CH$_2$C*H*$_2$CHP[C(CH$_3$)$_3$]$_2$), 2.53 (m, 2 H, C*H*$_2$CH$_2$CHP-[C(CH$_3$)$_3$]$_2$), 4.23 (m, 2 H, CH$_2$CH$_2$C*H*P[C(CH$_3$)$_3$]$_2$, C*H*$_{AR}$(Cr)), 4.89 (d, 1 H, J = 6.8 Hz, C*H*$_{AR}$(Cr)), 4.94 (d, 1 H, J = 5.9 Hz, C*H*$_{AR}$(Cr)), 7.07−7.14 (m, 6 H, *m/p*-C*H* Ph$_2$P), 7.43 (tm, 2 H, *o*-C*H* Ph$_2$P), 7.67 (m, 2 H, *o*-C*H* Ph$_2$P). ^{13}C NMR (125 MHz, C_6D_6): δ 26.39 (CH$_2$*C*H$_2$CHP[C(CH$_3$)$_3$]$_2$), 30.83 (d, $^3J_{CP}$ = 14.8 Hz, P[C(*C*H$_3$)$_3$]$_2$), 31.24 (d, $^3J_{CP}$ = 12.7 Hz, P[C(*C*H$_3$)$_3$]$_2$), 32.86 (*C*H$_2$CH$_2$CHP[C(CH$_3$)$_3$]$_2$), 33.48 (d, $^1J_{CP}$ = 40.0 Hz, P[*C*(CH$_3$)$_3$]$_2$), 34.69 (d, $^1J_{CP}$ = 27.4 Hz, P[*C*(CH$_3$)$_3$]$_2$), 41.95 (d, $^1J_{CP}$ = 36.8 Hz, CH$_2$CH$_2$*C*HP[C(CH$_3$)$_3$]$_2$), 89.79 (*C*H$_{AR}$(Cr)), 92.90 (*C*H$_{AR}$-(Cr)), 100.16 (*C*H$_{AR}$(Cr)), 100.43 (*C*$_{AR}$(Cr)), 109.61 (*C*$_{AR}$(Cr)), 127.16 (t, $^1J_{CP} \approx {}^3J_{CP}$ = 22.0 Hz, *ipso-C*$_{AR}$(Cr)), 128.66 (d, $^3J_{CP}$ = 6.5 Hz, *m*-*C*H Ph$_2$P), 129.90 (*p*-*C*H Ph$_2$P), 133.76 (d, $^2J_{CP}$ = 20.8 Hz, *o*-*C*H Ph$_2$P), 135.46 (d, $^2J_{CP}$ = 20.3 Hz, *o*-*C*H Ph$_2$P), 137.31 (dd, $^1J_{CP}$ = 9.9 Hz, *ipso-C* Ph$_2$P), 139.69 (m, *ipso-C* Ph$_2$P), 233.53 (*C*O). ^{31}P NMR (81 MHz, C_6D_6): δ 50.05 (d, J_{PP} = 89.7 Hz, α-P*t*Bu$_2$), −19.13 (d, J_{PP} = 87.9 Hz, *o*-PPh$_2$). IR ($CHCl_3$): ν_{CO} 1963, 1893 cm^{-1}. MS (CI, isobutane**;** *m/z*): 583 (M + H, 48%), 525 (M − C(CH$_3$)$_3$, 16%), 447 (M + HCr(CO)$_3$, 16%), 439 (20%), 147 (100%). Anal. Calcd for $C_{32}H_{36}CrO_3P_2$: H, 6.23; C, 65.97. Found: H, 6.24; C, 65.91. $[\alpha]_D^{RT}$ = −382.8° (*c* 0.18 in $CHCl_3$).

***anti*-[η^6-(*S,R*p)-1-(dicyclohexylphosphino)-7-(diphenylphosphino)indane]Cr(CO)$_3$ (*Anti*-(*S,R*p)-6c). *anti*-(*S,R*p)-5** (0.48 g of crude product, ∼1.0 mmol) was dissolved in dry acetone, and dicyclohexylphosphine (0.20 g, 1.0 mmol) was added. To this solution was added dropwise very slowly a suspension of $TlPF_6$ (0.35 g, 1.0 mmol) in dry acetone (final concentration of Cr in acetone [Cr] = 0.05 M). A fine white precipitate formed immediately. The solution was stirred at room temperature overnight. NEt_3 (1.5 mL) was added, and the solution was stirred for a further 15 min and then filtered through a short pad of Celite on a sintered-glass funnel to remove TlCl. The solvent and excess NEt_3 were distilled off, and the crude product was purified by column chromatography (aluminum oxide, neat hexane → diethyl ether/hexane 1/4), followed by crystallization from dichloromethane/hexane at −30 °C. Yield: 0.47 g (67%) over two steps from ***anti*-(*S,R*p)-4** (0.53 g, 1.1 mmol). R_f = 0.57 (aluminum oxide, hexane/diethyl ether 4/1). ^{1}H NMR (500 MHz, C_6D_6): δ 0.98−1.60 (ms, 19 H, P(C$_6$H$_{11}$)$_2$), 1.68 (ms, 2 H, P(C$_6$H$_{11}$)$_2$), 1.86 (m, 1 H, P(C$_6$H$_{11}$)$_2$), 1.95 (m, 1 H, CH$_2$C*H*$_2$CHP(C$_6$H$_{11}$)$_2$), 2.24 (m, 1 H, CH$_2$C*H*$_2$-CHP(C$_6$H$_{11}$)$_2$), 2.42 (m, 2 H, C*H*$_2$CH$_2$CHP(C$_6$H$_{11}$)$_2$), 4.09 (bd, 1H, J = 9.15 Hz, CH$_2$CH$_2$C*H*P(C$_6$H$_{11}$)$_2$), 4.19 (t, 1 H, J = 6.4 Hz, C*H*$_{AR}$(Cr)), 4.91 (d, 1 H, 6.4 Hz, C*H*$_{AR}$(Cr)), 4.98 (d, 1 H, J = 5.8 Hz, C*H*$_{AR}$(Cr)), 7.07 (bt, 2 H, J = 7.3 Hz, *p*-*C*H Ph$_2$P), 7.16 (m, 4 H, *m*-*C*H Ph$_2$P), 7.42 (bt, 2 H, J = 7.3 Hz, *o*-*C*H Ph$_2$P), 7.46 (bt, 2 H, J = 7.3 Hz, *o*-*C*H Ph$_2$P). ^{13}C NMR (125 MHz, C_6D_6): δ 26.67 (d, J_{CP} = 7.1 Hz, P(*C*$_6$H$_{11}$)$_2$), 26.83 (P(*C*$_6$H$_{11}$)$_2$), 27.22 (P(*C*$_6$H$_{11}$)$_2$), 27.56 (d, J_{CP} = 19.7 Hz, P(*C*$_6$H$_{11}$)$_2$), 27.53 (P(*C*$_6$H$_{11}$)$_2$), 29.37 (d, J_{CP} = 6.6 Hz, P(*C*$_6$H$_{11}$)$_2$), 29.78 (CH$_2$*C*H$_2$CHP(C$_6$H$_{11}$)$_2$), 30.19 (P(*C*$_6$H$_{11}$)$_2$), 31.96 (d, J_{CP} = 19.8 Hz, P(*C*$_6$H$_{11}$)$_2$), 32.92 (*C*H$_2$CH$_2$CHP(C$_6$H$_{11}$)$_2$), 33.38 (d, $^1J_{CP}$ = 24.1 Hz, *ipso*-P(*C*$_6$H$_{11}$)$_2$), 34.08 (d, $^1J_{CP}$ = 20.9 Hz, *ipso*-P(*C*$_6$H$_{11}$)$_2$), 39.72 (dd, $^1J_{CP}$ = 28.0 Hz, $^3J_{CP}$ = 7.1 Hz, CH$_2$-CH$_2$*C*HP(C$_6$H$_{11}$)$_2$), 89.32 (*C*H$_{AR}$(Cr)), 93.01 (*C*H$_{AR}$(Cr)), 99.82 (*C*H$_{AR}$(Cr)), 109.66 (*C*$_{AR}$(Cr)), 128.76 (d, $^3J_{CP}$ = 7.2 Hz, *m*-*C*H Ph$_2$P), 129.58 (*p*-*C*H Ph$_2$P), 133.66 (d, $^2J_{CP}$ = 18.1 Hz, *o*-*C*H

Ph_2P), 135.33 (d, $^2J_{CP}$ = 20.3 Hz, *o*-*C*H Ph_2P), 137.63 (m, *ipso*-*C*H Ph_2P), 139.31 (m, *ipso*-*C*H Ph_2P), 233.36 (*C*O). ^{31}P NMR (81 MHz, C_6D_6): δ 16.71 (d, J_{PP} = 64.1 Hz, α-PCy_2), −18.80 (d, J_{PP} = 65.9 Hz, *o*-PPh_2). IR ($CHCl_3$): ν_{CO} 1964, 1894 cm^{-1}. MS (EI**;** *m/z*): 634 (M^+, 69%), 550 (M − 3CO, 100%), 415 (M − Cr(CO)$_3$ − C_6H_{11}, 78%). Anal. Calcd for $C_{36}H_{40}CrO_3P_2$: H, 6.35; C, 68.13. Found: H, 6.20; C, 68.62. $[\alpha]_D^{RT}$ = +305.4° (*c* 0.22 in $CHCl_3$).

{**Rh(NBD)**{***anti*-[η^6-(***R*,*S*p),(***S*,*R*p)-1,7-bis(diphenylphosphino)indane]Cr(CO)$_3$}}**BF_4 (7a)** [Rh(NBD)$_2$]BF_4 (102.0 mg, 0.27 mmol) was dissolved in a 1:1 mixture of methanol and dichloromethane (15 mL). Upon the addition of ***anti*-6a** (102.0 mg, 0.27 mmol), the solution became deep orange and was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (3 mL). Addition of diethyl ether (30 mL) brought about precipitation of the product **7a**, which was filtered off, washed with diethyl ether, and dried in vacuo. The product was recrystallized from dichloromethane/diethyl ether at −30 °C. Yield: 145 mg (59%). ^{1}H NMR (500 MHz, CD_3COCD_3): δ 1.59 (m, 2 H, H_{NBD}), 1.64 (bd, 1 H, J_{HH} = 8.6 Hz, H_{NBD}), 1.81 (m, 1 H, CH(PPh_2)CH_2CH_2), 2.41 (m, 3 H, CH(PPh_2)C*H*$_2$CH$_2$, CH(PPh_2)CH_2C*H*$_2$), 3.83 (m, 1 H, C*H*(PPh_2)-CH_2CH_2), 3.99 (m, 2 H, H_{NBD}), 4.38 (bs, 1 H, H_{NBD}), 4.55 (bs, 1 H, H_{NBD}), 4.91 (bs, 1 H, H_{NBD}), 5.22 (bs, 1 H, H_{NBD}), 5.29 (bt, 1 H, J_{HH} = 6.41 Hz, C*H*$_{AR}$(Cr)), 5.94 (bd, 1 H, J_{HH} = 6.41 Hz, C*H*$_{AR}$(Cr)), 6.12 (bt, 1 H, $J_{HH} \approx J_{HP}$ = 6.41 Hz, C*H*$_{AR}$(Cr)), 7.57 (m, 4 H, C*H* PPh_2), 7.64 (ddd, 2 H, J_{HP} = 11.0 Hz, J_{HH} = 7.6 Hz, J_{HH} = 1.5 Hz, C*H* PPh_2), 7.73 (m, 6 H, C*H* PPh_2), 7.79 (m, 4 H, C*H* PPh_2), 7.97 (bdd, 2 H, J_{HP} = 11.0 Hz, J_{HH} = 7.6 Hz, C*H* PPh_2), 8.50 (ddd, 2H, J_{HP} = 12.5 Hz, J_{HH} = 7.6 Hz, J_{HH} = 1.5 Hz, C*H* PPh_2). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 26.95 (CH(PPh_2)*C*H$_2$CH$_2$), 30.88 (CH(PPh_2)CH$_2$*C*H$_2$), 40.69 (*C*H(PPh_2)-CH_2CH_2),), 54.96 (bs, C_{NBD}), 55.37 (bs, C_{NBD}), 71.07 (bs, C_{NBD}), 82.99 (bs, C_{NBD}), 86.27 (bs, C_{NBD}), 87.44 (d, $^3J_{CP}$ = 4.4 Hz, *C*H$_{AR}$(Cr)), 94.06 (bs, C_{NBD}), 94.32 (bs, C_{NBD}), 96.57 (*C*H$_{AR}$(Cr)), 101.16 (*C*H$_{AR}$(Cr)), 110.77 (*C*$_{AR}$(Cr)), 116.50 (*C*$_{AR}$(Cr)), 127.34 (d, $^1J_{CP}$ = 40.6 Hz, *ipso*-*C*$_{AR}$(Cr)), 127.60 (d, $^1J_{CP}$ = 44.0 Hz, *ipso*-*C*H Ph_2P), 130.34 (d, J_{CP} = 10.4 Hz, *C*H Ph_2P), 130.50 (d, J_{CP} = 7.2 Hz, *C*H Ph_2P), 130.60 (d, J_{CP} = 5.4 Hz, *C*H Ph_2P), 130.76 (d, J_{CP} = 9.3 Hz, *C*H Ph_2P), 131.79 (d, J_{CP} = 8.7 Hz, *C*H Ph_2P), 132.31 (d, J_{CP} = 7.7 Hz, *C*H Ph_2P), 133.20 (d, $^1J_{CP}$ = 50.3 Hz, *ipso*-*C*H Ph_2P), 133.68 (d, J_{CP} = 11.0 Hz, *C*H Ph_2P), 134.11 (d, J_{CP} = 9.9 Hz, *C*H Ph_2P), 136.36 (d, J_{CP} = 13.1 Hz, *C*H Ph_2P), 137.57 (d, J_{CP} = 15.4 Hz, *C*H Ph_2P), 232.18 (*C*O). ^{31}P NMR (81 MHz, CD_3COCD_3): δ 34.50 (dd, J_{PRh} = 155.7 Hz, J_{PP} = 40.3 Hz, *o*-PPh_2), 55.86 (dd, J_{PRh} = 157.5 Hz, J_{PP} = 40.3 Hz, α-PPh_2).

{**Rh(NBD)**{***anti*-[η^6-(***R*,*S*p)-1-(di-*tert*-butylphosphino)-7-(diphenylphosphino)indane]Cr(CO)$_3$}}**BF_4 (7b).** This complex was prepared in situ and was not isolated. [Rh(NBD)$_2$]-BF_4 (7.4 mg, 0.02 mmol) and **6b** (11.6 mg, 0.02 mmol) were dissolved in CD_3COCD_3 (2 mL). The resulting clear deep orange solution was stirred at room temperature for 2 h. After this time, in the ^{1}H NMR spectrum only the signals due to uncordinated norbornadiene and to the expected complex **7b** could be detected. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 1.55 ppm (m, J_{HP} = 13.6 Hz, 9H, *H* P*t*Bu_2), 1.60 (d, J_{HP} = 13.6 Hz, 10H, *H* P*t*Bu_2, H_{NBD}), 1.78 (m, 1 H, H_{NBD}), 2.58 (m, 1 H, C*H*$_{aliph}$), 2.96 (m, 1 H, C*H*$_{aliph}$), 3.06 (m, 1 H, C*H*$_{aliph}$), 3.24 (m, 1 H, C*H*$_{aliph}$), 3.53−3.59 (m, 2H, H_{NBD}, C*H*$_{aliph}$), 3.85 (bs, 1H, H_{NBD}), 4.15 (bs, 1H, H_{NBD}), 5.40 (t, J_{HH} = 6.4 Hz, C*H*$_{AR}$(Cr)), 5.97 (bs, 1H, H_{NBD}), 6.07 (t, J_{HH} = 6.4 Hz, C*H*$_{AR}$(Cr)), 6.22 (d, J_{HH} = 6.4 Hz, C*H*$_{AR}$(Cr)), 6.36 (bs, 1H, H_{NBD}), 7.37−7.42 (m, 2H, *o*-C*H* PPh_2), 7.59−7.65 (m, 4H, *m*/*p*-C*H* PPh_2), 7.70−7.76 (m, 4H, *m*/*p*-C*H* PPh_2), 8.57−6.23 (m, 2H, *o*-C*H* PPh_2). ^{31}P NMR (162 MHz, CD_3COCD_3): δ 37.70 (dd, J_{PRh} = 160.1 Hz, J_{PP} = 37.6 Hz, *o*-PPh_2), 74.28 (dd, J_{PRh} = 147.6 Hz, J_{PP} = 37.6 Hz, α-P*t*Bu_2).

{**Rh(NBD)**{***anti*-[η^6-(***S*,*R*p)-1-(dicyclohexylphosphino)-7-(diphenylphosphino)indane]Cr(CO)$_3$}}**BF_4 (7c).** This complex was prepared in situ and was not isolated. [Rh(NBD)$_2$]BF_4 (7.4 mg, 0.02 mmol) and **6c** (12.6 mg, 0.02 mmol) were dissolved in CD_3COCD_3 (2 mL). The resulting clear deep orange solution was stirred at room temperature for 2 h. After this time, in the ^{1}H NMR spectrum only the signals due to uncoordinated norbornadiene and to the expected complex **7c** could be detected. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 0.88−2.06 ppm (m, H, −PCy), 2.32 (m, 1H, −PCy), 2.43 (m, 1H, −PCy), 2.52 (m, 1 H, C*H*$_{aliph}$), 2.74 (m, 1 H, C*H*$_{aliph}$), 2.96 (m, 1 H, C*H*$_{aliph}$), 3.25 (m, 1 H, C*H*$_{aliph}$), 3.42 (m, 1 H, C*H*$_{aliph}$), 3.78 (bs, 1H, H_{NBD}), 4.03 (bs, 1H, H_{NBD}), 4.26 (bs, 1H, H_{NBD}), 4.69 (bs, 1H, H_{NBD}), 5.42 (t, 1 H, J_{HH} = 6.4 Hz, C*H*$_{AR}$(Cr)), 5.87 (bs, 1H, H_{NBD}), 6.13 (t, 1 H, J_{HH} = 6.2 Hz, C*H*$_{AR}$(Cr)), 6.20 (bs, 1H, H_{NBD}), 6.31 (d, 1 H, J_{HH} = 6.6 Hz, C*H*$_{AR}$(Cr)), 7.45 (m, 2H, *o*-C*H* PPh_2), 7.70 (m, 4H, *m*/*p*-C*H* PPh_2), 7.77 (m, 4H, *m*/*p*-C*H* PPh_2), 8.52 (m, 2H, *o*-C*H* PPh_2). ^{31}P NMR (162 MHz, CD_3COCD_3): δ 33.33 (dd, J_{PRh} = 158.5).

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Supporting Information Available: Tables of crystal data and structure solution and refinement details, atomic coordinates, anisotropic thermal parameters, interatomic distances and angles, and hydrogen atom coordinates, figures giving additional views, and CIF files for ***syn*-(*S*,*S*p)-4** and ***anti*-(*S*,*R*p)-6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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