Induction of Planar Chirality in Formation of (η^5:η^1-1-(1-Cyclohexyl-2-(diphenylphosphino)ethyl)indenyl)-carbonylrhodium and (η^5:η^1-1-(2-Phenyl-2-(diphenylphosphino)ethyl)indenyl)carbonylrhodium

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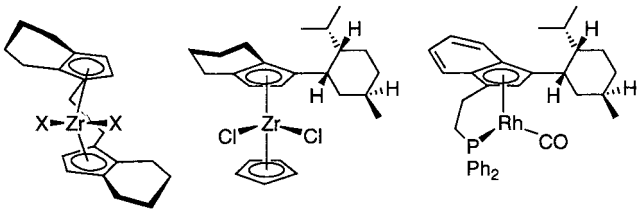
The enantiopure bidentate indenyl−phosphine ligands (1*S*)-[2-(3*H*-inden-1-yl)-1-phenylethyl]diphenylphosphine (**9**) and [(2*R*)-2-cyclohexyl-2-(3*H*-inden-1-yl)ethyl]diphenylphosphine (**18**) were synthesized in 20% yield and three steps from (*R*)-styrene oxide and in 61% yield and four steps from vinylcyclohexane, respectively. In both cases ring opening of a spirocyclopropane-1,1′-indene with potassium diphenylphosphide was a key step. Addition of the lithium salts of **9** and **18** to $[Rh(\mu\text{-}Cl)(CO)_2]_2$ gave (η^5:η^1-indenyl-$CH_2CH(Ph)PPh_2$)RhCO and (η^5:η^1-indenyl-$CH(Cy)CH_2PPh_2$)RhCO as 75:25 and 78:22 mixtures of diastereoisomers, from which the major complexes were readily obtained by crystallization. The chiral centers in the linking chain β and α to the indenyl ring had thus induced good planar chirality of the complexed indenyl moiety. Both complexes were characterized by X-ray crystallography.

Introduction

The development of chiral transition-metal catalysts for asymmetric transformations has been one of the most significant advances in synthetic organic chemistry over the past decade.[1] Most have been based on bisphosphine or bis-alkoxide ligands (usually C_2 symmetric), with recent interest in less symmetric systems such as aminophosphines.[1] The most common ligand in transition-metal chemistry is η^5-cyclopentadienyl (and related substituted and indenyl versions), and there have been many attempts to develop effective chiral versions, with limited success.[2−9] For efficient transfer of chirality from a metal complex to a substrate the source of chirality needs to be close to the metal center. The best prospect for this with η^5-cyclopentadienyl complexes is when the cyclopentadiene is nonsymmetrically substituted, thus generating planar chirality on coordination to the metal. The most successful chiral cyclopentadienyl complexes to date, the *ansa*-metallocenes (e.g. **1**), are illustrative.[4]



1 **2** **3**

A problem with **1** is that the ligand used in the complexation, 1,2-bis(indenyl)ethane, is achiral; thus, coordination of the metal to the enantiofaces of the indenyl moieties is nonselective, resulting in a racemic complex (as well as a meso form). A solution would be

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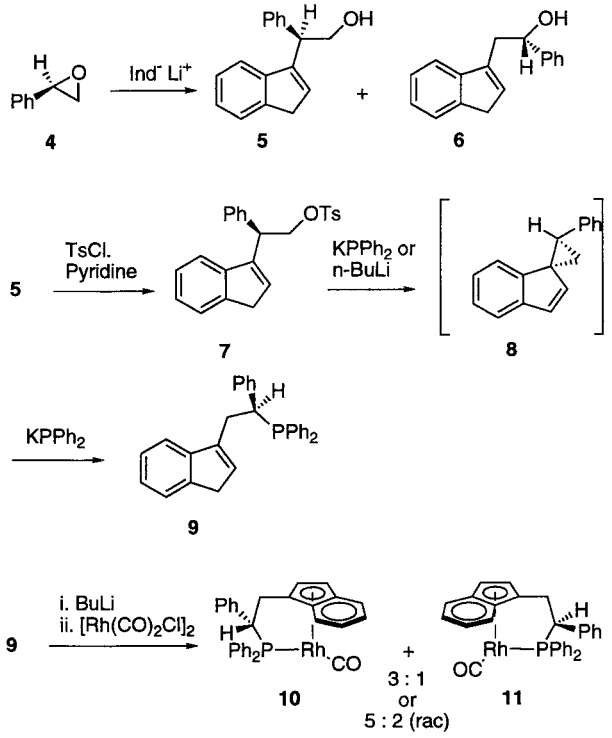
to use a chiral group in the ligand to direct selective metalation of one enantioface of a nonsymmetrically substituted cyclopentadiene. For *ansa*-metallocenes of titanium and zirconium incorporation of a chiral center in the connecting chain[5] and replacement of the saturated ring of the tetrahydroindenyl moiety with a chiral bridged bicyclic system have been successful.[6]

For unlinked cyclopentadienes (and thus potentially applicable to monocyclopentadienyl complexes) the 3-neomenthylindenyl ligand introduced by Erker[7] and used by us in the synthesis of complex **2**[8] is particularly significant. The neomenthyl group provides good "induction of planar chirality" (6:1 dr) on complexation to zirconium. The complex **2** gives good enantiomeric inductions when used as a catalyst for ethylmagnesiation and 2-aluminoethylalumination reactions.[8] Fusion of a chiral bridged bicyclic system to a cyclopentadiene provides another method for enantiofacially directed metalation.[9]

We wished to extend our studies on "planar chiral" complexes to monocyclopentadienyl complexes of later transition metals. A few chiral monocyclopentadienyl complexes of rhodium, ruthenium, cobalt, and iron are known but give low enantioinductions in catalyzed reactions.[10] Ferrocenes containing planar-chiral cyclopentadienes are well-known and have generally been produced by elaboration of the ligand after formation of the complex.[11] To provide orientation on the metal, we chose to investigate complexes of bidentate linked phosphine−indene ligands. Our aim was to direct the metal to one enantioface of the indene using a chiral center in the connecting chain (induction of planar chirality).

Linked cyclopentadienyl−phosphine metal complexes have been recently reviewed.[12] The only use of linked indenyl−phosphine ligands has been for some rhodium complexes recently reported by Tani.[13] Examples of linked cyclopentadiene−phosphine ligands with chiral centers in the connecting chain are known,[14] but not where induction of planar chirality on complexation of the cyclopentadiene to the metal is a feature.[15] Recently Tani reported the 1-neomenthyl-3-(2-(diphenylphosphino)ethyl)indenyl ligand, where (as with **2**) the neomenthyl group directs enantiofacially selective metalation to afford the complex **3**.[16]

Scheme 1



We now report the synthesis of the novel bidentate indenyl−phosphine ligands **9** and **18** and their rhodium(I) carbonyl complexes, in which a chiral center in the linking chain induces selective complexation of the metal to one enantioface of the indene.

Results and Discussion

Synthesis and Complexation of a Ligand with a Chiral Center α to Phosphorus. Reaction of styrene oxide (**4**) (commercially available as either enantiomer) with indenyllithium according to the method of Reiger[17] affords a 3:2 mixture of the readily separated alcohols **5** and **6**[18] (Scheme 1). Tosylation of **5** followed by reaction with potassium diphenylphosphide (14 h, 20 °C) gave the rearranged ligand **9**. The regiochemistry of ring opening was indicated by the chemical shifts and couplings to phosphorus of the CHPh (δ_C 44.0 ppm, J_{CP} = 14 Hz) and CH_2Ind (δ_C 31.7 ppm, J_{CP} = 24 Hz) carbons. It is usual for $^2J_{CP} > {}^1J_{CP}$ in similar systems.[19] Further confirmation came from the observation of long-range correlation between the alkyl chain CH_2 protons and the vinyl CH carbon on the indenyl ring. A reason-

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(15) Tani reported complexation of [5-(3*H*-inden-1-ylmethyl)-2,2-dimethyl[1,3]dioxolan-4-ylmethyl]diphenylphosphane to [Rh(μ-Cl)$(CO)_2]_2$ to give a 69:31 mixture of diastereoisomers.[14a] Trost reported[14b] a variety of ruthenium complexes of 3-benzylcyclopentadienes attached through a four-carbon chain containing chiral substituents to a diphenylphosphine group. The best mixture of diastereoisomers obtained was 1.6:1.

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(18) Reiger reports[17] obtaining just the alcohol **5** in 67% yield, although the proton NMR data he gives is only consistent with **6**. Since ring closure to the spiroindene **8** gives the same product from either isomeric alcohol, the mixture could be used, although we found that tosylation of **6** was slow and mesylation preferable.

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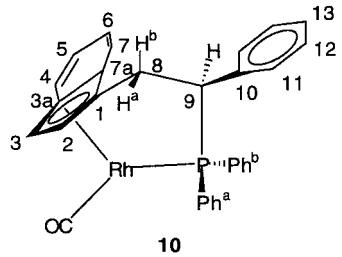
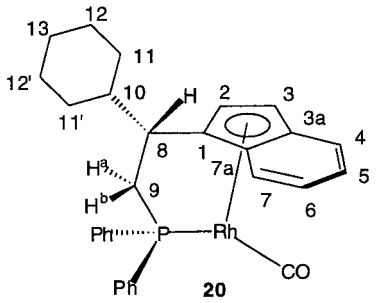
able explanation for the unexpected regiochemistry of **9** arises from the initial formation of the spirocycle **8** via deprotonation of the indenyl ligand by the diphenylphosphide and ring closure. Attack on **8** by diphenylphosphide at the activated benzylic position would then afford **9**.[20] Support for this mechanism came from treatment of a solution of **7** with *n*-butyllithium to afford **8** as a single diastereoisomer, confirmed to be as shown by X-ray crystallography.[21] Spiroindene **8** was then opened efficiently by potassium diphenylphosphide to afford **9**. Selective attack at the benzylic position of **8** by cyclopentadienide has been previously noted.[17] After completion of this work Salzer reported the same regiochemistry in opening 2-phenylspiro[2.4]hepta-4,6-diene with diphenylphosphide.[22] It is interesting that we get complete conversion of **7** into **9** using 1.1 equiv of Ph_2PK, indicating a catalytic cycle in which the indenyl anion formed by diphenylphosphide opening of **8** deprotonates the Ph_2PH formed in the initial deprotonation of **7**.

The (*S*)-indenyl phosphine **9** was treated with *n*-butyllithium in THF and the deep red solution added to a golden yellow solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in THF at −78 °C. The addition resulted in a dark brown solution which was warmed to room temperature overnight. ^{1}H NMR analysis of the crude product revealed the formation of a rhodium(I) indenyl complex as a 3:1 mixture of the diastereoisomers **10** and **11**. The racemic ligand gave a 5:2 mixture. Purification of the complex was achieved by column chromatography on neutral alumina to give a mixture of the complexes as a yellow powder in an excellent 71% yield. The diastereoisomerically pure complex **10** was isolated by recrystallization from diethyl ether/hexanes in 30% overall yield. IR and ^{13}C NMR spectroscopy confirmed the presence of the carbonyl group with ν_{CO} at 1946 cm^{-1} and a doublet of doublets (J_{CRh} = 89 Hz, J_{CP} = 17 Hz) in the ^{13}C NMR spectrum at 191 ppm, characteristic of a carbonyl group bound to rhodium.[13] Analysis of the proton-decoupled ^{31}P NMR spectrum showed a doublet at 86.2 ppm with J_{PRh} = 214 Hz, indicative of a phosphorus attached to a rhodium(I) center.[23] The large downfield shift of the phosphorus signal to 86.2 ppm is characteristic of the formation of a five-membered chelate ring,[23] lending support to the proposed structure of **10**. The increase in $^1J_{PC}$ to the attached phenyl rings from ∼16 Hz in the free ligand to ∼40 Hz in the complex is also indicative in an increase in coordination number around phosphorus from 3 to 4.[24] The proton and carbon NMR of **10** was fully assigned using H−H COSY, long- and short-range carbon−proton correlation (HMBC and HMQC), and NOESY spectra in both $CDCl_3$ and C_6D_6. Comparison of carbon-13 spectra at 100 and 75 MHz allowed splittings due to chemical shift differences and coupling to phosphorus or rhodium to be unambiguously distinguished. The results are shown in Table 1. The proton NMR of **10** contained items of note relating to stereochemistry. One is that one of the diastereotopic bridge CH_2− protons (H8^b) shows $^4J_{PH}$ = 63 Hz coupling to phosphorus (confirmed in the proton-coupled phosphorus NMR). For comparison, the other CH_2 proton (H8^a) and the CHPh proton show couplings of 14 Hz to the

Table 1. NMR Assignments for 10 and 20



10



20

10				**20**			
	δ_C	J_{CP}[a]	J_{CRh}[a]		δ_C	J_{CP}[a]	J_{CRh}[a]
CO	190.29	17	89	CO	191.26	17.9	88.4
o-Ph[a]	137.53	13.5	1	*o*-Ph	134.48	13.8	1.0
i-Ph	135.3	39.5	1	*i*-Ph	134.42	38.4	1.0
o-Ph[b]	131.95	10.5		*o*-Ph	131.72	11.6	1.2
p-Ph[a]	131.05	2.2		*p*-Ph	130.52	2.4	
i-Ph	130.0	42.1	3.2	*i*-Ph	136.25	44.6	3.5
p-Ph[b]	129.64	2.8		*p*-Ph	129.82	2.4	
m-Ph[b]	128.48	10		*m*-Ph	128.50	10.4	
m-Ph[a]	127.61	11.5		*m*-Ph	128.44	10.6	
6	124.31			6	124.37	0.7	
5	121.91			5	121.09		
3a	120.95	1.0		3a	116.41	2.3	1.4
4	118.46	1.6		4	117.92	1.2	
7	117.13			7	117.42		
7a	116.1	2.1	1.6	7a	116.08	1.1	0.9
2	98.4	5.6	4.0	2	91.36	5.6	3.1
1	92.1	4.8	3.7	1	103.23	5.0	3.8
3	72.4	10.8	3.2	3	76.09	10.6	3.6
9	67.77	18.4		9	52.60	29.7	
8	30.46	9		8	39.37	4.8	
10	137.8	9.5	1	10	42.95	22.4	
12	128.36	3.0		11/11′	33.56		
11	128.20	2.2		11/11′	31.17		
13	127.37	2.2		12/12′/13	26.58		
				12/12′/13	26.42		
				12/12′/13	26.25		

10			**20**			
	δ_H	J_{HP}		δ_H	J_{HP}	J_{HRh}
H-8[a]	2.636	14	H-8	2.63	9.0	
H-8[b]	2.813	62.3	H-9[a]	2.93	7.0	
H-9	5.552	14	H-9[b]	3.30	13.3	2.5

[a] J_{CP} and J_{CRh} may be interchanged; the assignment is based only on expected values.

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(21) Crystal data: $C_{17}H_{14}$, M_r = 218.28, monoclinic, space group $P2_1/c$, a = 6.9761(14) Å, b = 12.498(3) Å, c = 14.135(3) Å, β = 93.36(3)°, V = 1230.3(4) Å^3, Z = 4, T = 150 K, 9994 measured/2794 independent reflections, R(int) = 0.0458. The final R1 and wR2 values were 0.0516 and 0.1216 (0.0802, 0.1390, all data). This structure report will be published elsewhere.

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Table 2. Crystallographic Data for 10 and 20

	10	**20**
empirical formula	$C_{30}H_{24}OPRh$	$C_{30}H_{30}OPRh$
fw	534.4	540.4
cryst syst	monoclinic	orthorhombic
space group	$P2_1$	*Pbca*
a (Å)	8.6414(2)	17.055(3)
b (Å)	24.6807(5)	16.304(3)
c (Å)	11.1050(3)	17.645(4)
β (deg)	92.6787(1)	
V (Å^3)	2365.84(10)	4906.5(17)
Z	4	8
D_{calcd} (g cm^{-3})	1.500	1.463
μ(Mo Kα) (mm^{-1})	0.810	0.782
cryst size (mm)	0.4 × 0.3 × 0.25	0.1 × 0.05 × 0.05
F_{000}	1088	2224
temp (K)	150(2)	150(2)
no. of measd rflns	31 633	31 323
no. of unique rflns	10359 (R_{int} = 0.055)	5617 (R_{int} = 0.1083)
no. of observns ($I > 2\sigma(I)$)	9443	3416
no. of variables	595	298
residuals: *R*; R_w[a]	0.0444; 0.0995	0.0432; 0.0764
ρ_{max}/ρ_{min} (e Å^{-3})	2.55[b]/−0.755	0.750/−0.620
goodness of fit on F^2	1.083	0.945

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$. [b] A ripple peak located 1.03 Å from Rh with no structural meaning.

phosphorus. The exceptionally high 63 Hz coupling presumably reflects a close to 180° dihedral angle for PCC(H8[b]). H8[a] also shows NOE correlations to the indenyl proton on C2. For comparison, H8[b] shows an NOE to H9 and that of H9 to H7 on the indenyl moiety. Taken together, these observations confirm the relative configurations of the side chain chiral center and the planar chirality of the indenyl ring. NOE correlations between both H2 and H8[a] and the ortho protons on one of the phenyl rings attached to phosphorus allowed this to be identified as Ph[a]. A notable long-range coupling is $^5J_{CP}$ = 2.2 Hz to C13, probably due to the close alignment of the P−CHPh bond with the aromatic π system. Rhodium shows $^1J_{CRh}$ = 1−6 Hz to the cyclopentadienyl carbons,[25] $^2J_{CRh}$ = 1 and 3.2 Hz to the ipso P−Ph carbons, and a notable $^3J_{CRh}$ = 1 Hz to C10, presumably reflecting a close to 180° RhPC(C10) dihedral angle.

Slow crystallization of (*S*,*S*)-**10** from pentane−ether gave red cubic crystals suitable for X-ray crystallography. Details of the crystal structure determination are given in Table 2, an ORTEP picture is given in Figure 1, and important geometric parameters are given in Table 3. It was interesting to confirm the near 180° dihedral angle PCC(H8[b]) and RhPC(C10) predicted by the proton−phosphorus and carbon−rhodium coupling constants described above. The indenyl ring shows a similar distortion toward η^3 coordination as (Ind)Rh(CO)$_2$[26a] and (Ind)Rh(PMe$_3$)$_2$,[26b] the bonds between rhodium and the benzene-ring-fused cyclopentadienyl carbons being around 0.2 Å longer than the others. The chelate ring causes some tilting of the cyclopentadiene (Rh−C(1) is 0.09 Å shorter than Rh−C(3)), and the Cp(centroid)−Rh−P angle (118.0°) is much smaller than in CpRh(PPh$_3$)(CO)[27] (134.8°)—effects also observed in

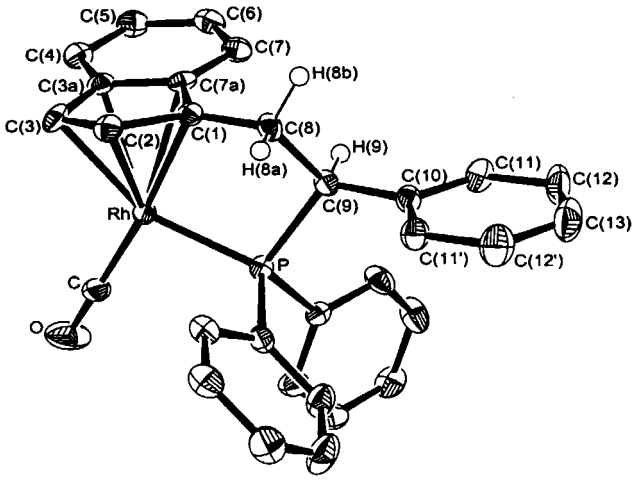

Figure 1. ORTEP view of the molecular structure of **10**. Thermal ellipsoids are drawn at 50% probability.

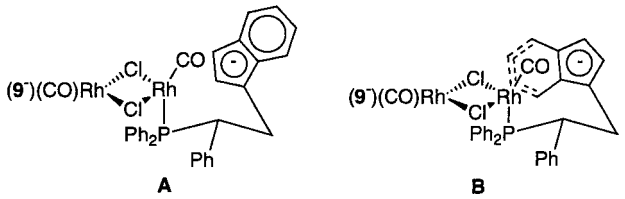

Figure 2. Possible transition states for the formation of **10** and **11**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 10 and 20

	10	**20**
Rh−C(1)	2.171(5)	2.179(3)
Rh−C(2)	2.240(5)	2.227(3)
Rh−C(3)	2.267(5)	2.261(3)
Rh−C(3a)	2.448(5)	2.433(3)
Rh−C(7a)	2.381(5)	2.395(3)
Rh−P	2.241(1)	2.2226(9)
Rh−CO	1.843(6)	1.836(4)
$Cp_{centroid}$−Rh−P	118.0	116.9
Rh−P−C(9)−C(10)	165.1(4)	
Rh−P−C(9)−H(9a)		162.9(2)
P−C(9)−C(8)−H(8a)	74.6(5)	
P−C(9)−C(8)−H(8b)	167.6(4)	
P−C(9)−C(8)−C(10)		166.9(2)
P−C(9)−C(8)−H(8)		74.57(3)

$C_5H_4(CH_2)_2PPh_2Rh(CH_2{=}CH_2)$,[23a] ($C_5H_4SiMe_2CH_2PPh_2$)Rh(CO),[23b] and ($C_5H_4CH_2CHPhPPh_2$)Rh($CH_2{=}CH_2$).[22]

We were surprised to achieve such a high level of induction of planar chirality with the inducing center remote to the indenyl ring. The most likely explanation is that complexation of phosphine to the rhodium precedes chloride displacement by the metalated indene, as suggested by Poilblanc for complexation of [Cp(CH$_2$)$_2$PPh$_2$]$^-$ to [Rh(μ-Cl)CO$_2$]$_2$.[23a] Since chloride displacement then takes place via a cyclic transition state, perhaps resembling Figure 2 (**A** leads to **10**), the substantial effect of the phenyl substituent is reasonable.[28] Poilblanc further suggests that two ligands bind to the rhodium dimer before chloride displacement, which could explain the small but consistent difference in facial selectivity observed with the chiral and racemic ligands (3:1; cf. 5:2 for **10** and **11**, respectively). The use

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(26) (a) Kakkar, A. K.; Taylor, N. J.; Calabrese, J. C.; Nugent, W. A.; Roe, D. C.; Connaway, E. A.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 990−992. (b) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012−2014.

(27) Choi, M.-G.; Brown, T. L. *Inorg. Chem.* **1993**, *32*, 5603−5610.

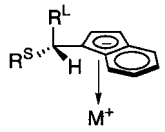
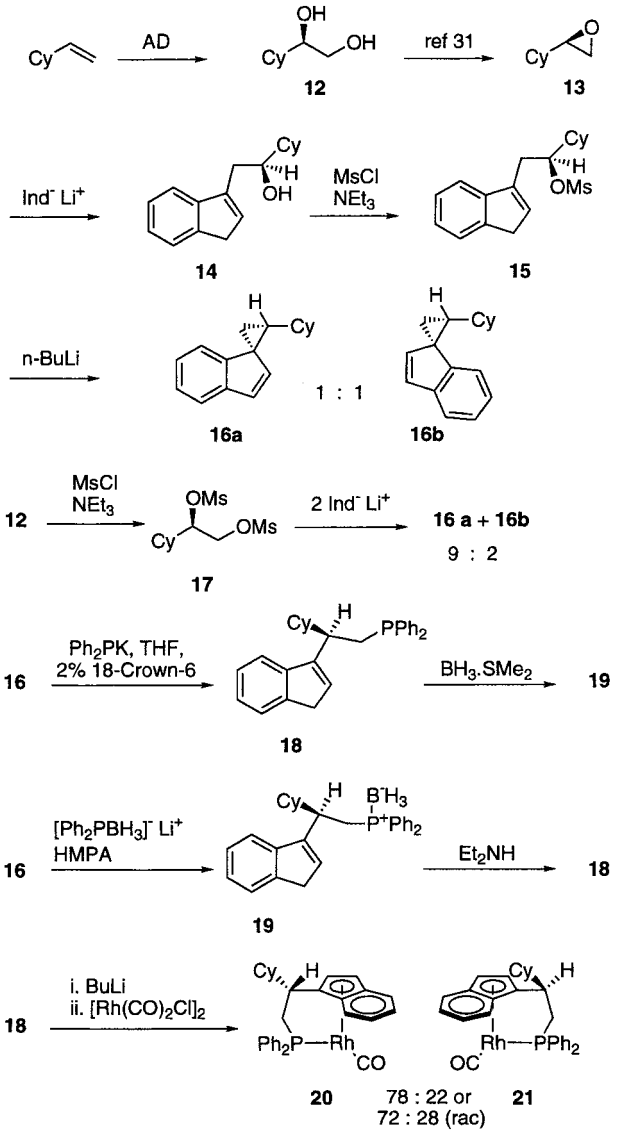


Figure 3. "Favored rotamer" model for induction of planar chirality.

of an initially formed zirconium−alkoxide bond has been used by Baker to direct metalation to one enantioface of an indene.[29]

Synthesis and Complexation of a Ligand with a Chiral Center α to the Indene. In complexation of 3-neomenthylindene to zirconium[7,8] and rhodium,[30] and in the formation of **3**,[16] high induction of planar chirality is observed. Related indenes such as 3-(1-phenylethyl)-indene, with a chiral center adjacent to the indenyl ring, also give good diastereoinduction.[30] The mechanism of enantiofacial induction is thought to be that in the favored rotamer of the indenyl−chiral substituent bond the two faces of the indenyl ring are differentially blocked by the large (R^L) and small (R^S) substituents (Figure 3).[7,8] This model predicts that a linked indenyl−phosphine ligand with a substituent adjacent to the indenyl ring should give good induction of planar chirality on complexation. Intramolecular delivery of the indene after prior coordination of the phosphine does not change the prediction, although the transition states are more complex. A suitable ligand should be available by diphenylphosphide opening of an alkyl-substituted 1,1-spirocyclopropylindene at the less hindered end—the expected regiochemistry when benzylic activation is not a factor. Our synthesis of a suitable ligand **18** to test the hypothesis started with vinylcyclohexane (Scheme 2). Epoxidation with *m*-chloroperbenzoic acid gave the racemic epoxide **13**. The (*R*)-epoxide **13** was synthesized[31] from the (*R*)-diol **12**, formed in 97% enantiomeric excess by Sharpless asymmetric dihydroxylation of vinylcyclohexane.[32] Ring opening of **13** with the indenyl anion gave the highly crystalline alcohol **14**, the optically active form of which was readily recrystallized to >99% ee. Tosylation of **14** proved difficult, but mesylation to afford **15** occurred readily. Ring closure by addition of *n*-butyllithium at −78 °C gave the spirocyclopropane as a 1:1 mixture of diastereoisomers **16a** and **16b**. Although this route gave the chiral spirocyclopropane **16** in excellent enantiomeric excess, due to recrystallization of the alcohol **14** it took five steps and gave only 30% overall yield from vinylcyclohexane.

Scheme 2



In the search for a more efficient method, we formed the crystalline bis-mesylate **17** from **12** in 97% yield. Unfortunately recrystallization of **17** did not enhance the enantiomeric excess. Addition of indenyllithium to a suspension of the bis-mesylate **17** in THF at 0 °C followed by 1 equiv of *n*-butyllithium gave the spirocycle **16** in moderate yield, surprisingly as a 9:2 mixture of isomers. A variety of other conditions and bases were tried for the cyclization, and the highest yields were obtained when the bis-mesylate **17** was added as a solid to a solution of 2.4 equiv of indenyllithium (acting as both the nucleophile and base) in THF at 0 °C. These conditions gave the spirocycle **16** (9:2 ratio **a**:**b**) as a white crystalline solid in 84% yield after chromatography, and removal of excess indene under vacuum.[33] The difference in ratios of **16a** to **16b** from the two synthetic routes (9:2 from **17**, 1:1 from **15**) is surprising, since the reaction of **17** presumably occurs via **15**, although the 1*H*-indenyl tautomer will be first formed. The difference in temperature used (0 °C; cf. −78 °C) is not responsible. The major isomer could be obtained pure by recrystal-

(28) Assuming a chair-like transition state, that leading to **11** would have either the phenyl group in an axial position and the aryl ring part of the indenyl moiety eclipsing the CO ligand (as in **A**) or the phenyl equatorial and the aryl ring part of the indenyl moiety eclipsing the ClRh(**9**) fragment. The latter seems more likely and is shown as **B** in Figure 2, but both should be less favorable than **A**. It is also possible (on the basis of ref 23a) that delivery of the indenyl moiety takes place at the rhodium opposite to that to which the phosphine is bound. The transition states are then more complex, but the essential point, that in a cyclic transition state substituents anywhere along the connecting chain have a substantial effect on the conformation and hence energies, remains.

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(33) After completion of this work Salzer reported a similar route to 2-phenylspiro[2,4]hepta-4,6-diene.[22]

lization from ethanol, but we have not yet proven its structure—that shown is by analogy to **8**. Cyclopropane **16** of 97% ee was thus available in three steps and 69% overall yield from vinylcyclohexane.

With large amounts of the cyclopropane **16** in hand, we examined the ring opening with diphenylphosphide anion. Under the conditions used to open **8** (Ph_2PK, THF, room temperature), little reaction occurred, but raising the temperature to reflux gave 80% conversion after 4 h. Most convenient, however, was to use Ph_2PK in THF with 2 mol % of 18-crown-6, under which conditions the reaction reached completion after 38 h at room temperature giving an excellent yield of the air-sensitive phosphine **18** after chromatography on silica under argon. For analysis, and convenience of storage and weighing, the crystalline, air-stable borane adduct **19** could be formed by reaction of **18** with $BH_3{\cdot}SMe_2$ at 0 °C.[34] It was important to control the temperature to avoid hydroboration of the indene double bond. The ligand **18** could be quantitatively liberated from the borane adduct **19** by refluxing with diethylamine.[34] To avoid handling the air-sensitive phosphine **18**, we found that the spirocycle **16** could be opened directly to give **19** with the borane adduct of lithium diphenylphosphide[35] in the presence of HMPA, although the yield was lower than using uncomplexed diphenylphosphide.

Deprotonation of **18** with *n*-butyllithium followed by addition to a solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in THF at −78 °C, warming to room temperature overnight, and removal of solvent gave the crude complex as a 78:22 mixture of **20** and **21**. Racemic ligand gave a 72:28 ratio. Purification by column chromatography (neutral alumina, 50% petrol/toluene) gave a mixture of **20** and **21** as an orange powder (68%). Recrystallization from diethyl ether/hexane at −30 °C afforded the major diastereoisomer **20** as clear red crystals (36%).

As expected, the NMR of **20** closely resembled that of **10** (Table 1), with similar C−Rh and C−P couplings establishing the basic structure. Interesting features of the NMR which relate to the stereostructure of **20** include $^4J_{CP} = 22.4$ Hz to C10 and $^4J_{RhH} = 2.5$ Hz to $H9^b$, both presumably reflecting close to 180° dihedral angles. Crystals of *rac*-**20** suitable for X-ray crystallography resulted from the standard purification procedure. Details of the crystal structure determination are given in Table 2, an ORTEP picture is given in Figure 4, and important bond lengths and angles are given in Table 3. The X-ray structure confirmed the relative stereochemistry of **20** and the dihedral angles, predicted from the NMR spectra. Otherwise, the structure is similar to that of **10** as discussed above. The main difference is that the connecting chain twists in opposite ways (relative to the indenyl ring) for the two compounds **10** and **20**.

Conclusion

We have developed efficient synthetic routes to the novel ligand types **9** and **18** and formed their rhodium carbonyl complexes. The ligands and complexes demonstrate an important principle of chiral complex design—that of induction of planar chirality on complexation of a nonsymmetrically substituted cyclopentadiene induced by a chiral center in a chain connecting to a second coordinating group. These ligands should find use with a variety of metals.

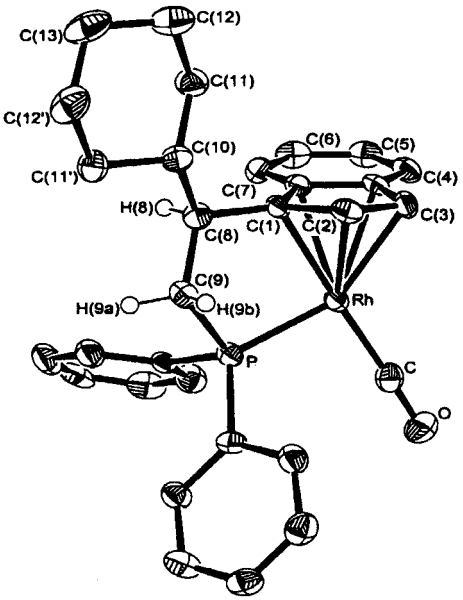

Figure 4. ORTEP view of the molecular structure of **20**. Thermal ellipsoids are drawn at 50% probability.

Experimental Section

General Procedures. All experiments were carried out under an argon atmosphere. Diisopropyl ether, diethyl ether, and tetrahydrofuran were freshly distilled from dark purple solutions of sodium/benzophenone ketyl under an argon atmosphere. Dichloromethane, pyridine, triethylamine, diethylamine, and hexamethylphosphoramide (HMPA) were dried over, and distilled from, calcium hydride. Petrol refers to the fraction of petroleum ether which boils between 40 and 60 °C and was redistilled before use. Potassium diphenylphosphide (0.5 M solution in THF) was purchased from Aldrich. Tetracarbonylbis(μ-chloro)dirhodium(I) was prepared from rhodium trichloride trihydrate.[36] (*R*)-1-Cyclohexylethane-1,2-diol (**12**) was prepared by Sharpless asymmetric dihydroxylation of vinylcyclohexane using the $(DHQD)_2PYR$ ligand[32] to give an 85% yield of material of 97% ee determined by HPLC resolution of its benzaldehyde acetal. (*R*)-2-Cyclohexyloxirane (**13**) was prepared in 77% yield by the Sharpless method[31] from (*R*)-1-cyclohexylethane-1,2-diol (**12**) and had spectroscopic properties and optical rotations in accord with those previously reported. ^1H and ^{13}C NMR spectra were referenced to TMS or residual protonated solvent (^1H NMR) or to deuterated solvent (^{13}C NMR). The number of attached protons in ^{13}C spectra was determined by DEPT experiments. ^{31}P NMR spectra were recorded proton-decoupled and referenced to external 85% H_3PO_4. Electron impact (EI) mass spectra were recorded at 70 eV. Atmospheric pressure ionization (AP^+) and Electrospray (ES^+) mass spectra were recorded on a VG Platform spectrometer using acetonitrile as the solvent and a positively charged cone.

Synthesis of (2*R*)-2-(3*H*-Inden-1-yl)-2-phenylethanol (5) and (1*S*)-2-(3*H*-Inden-1-yl)-1-phenylethanol (6). A solution of indene (5.8 g, 50 mmol) in diisopropyl ether (70

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mL) was cooled to −78 °C and *n*-BuLi (20.0 mL, 2.5 M solution in hexanes, 50 mmol) added dropwise. The resulting yellow suspension was stirred at −78 °C for 15 min and then warmed to room temperature and stirred for 2 h. The red suspension was cooled to 0 °C and (*R*)-(+)-styrene oxide (5.0 g, 41.6 mmol) added dropwise, maintaining the internal temperature at 0 °C. The mixture was stirred at 0 °C for 6 h and at room temperature for a further 16 h. A saturated solution of ammonium chloride (100 mL) was added and the product extracted into diethyl ether (3 × 75 mL). The combined organic layers were washed with brine (2 × 50 mL) and dried over $MgSO_4$ and the solvents removed in vacuo. Column chromatography (SiO_2, 5% Et_2O/toluene) gave the title alcohol **6** (2.40 g, 24.4%) followed by **5** (3.696 g, 37.6%) as pale yellow viscous oils. In the racemic series **5** was obtained as a white crystalline solid from pentane at 0 °C (mp 61−63 °C). The proton NMR of **6** is consistent with that reported for **5** by Rieger.[17,18]

Alcohol **5**: $[\alpha]_D^{20} = -13.5$ ($c = 0.96$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (1H, m), 7.37−7.30 (4H, m), 7.24 (1H, m), 7.20−7.15 (3H, m), 6.48 (1H, ddd, J = 2.0, 2.0, 1.3 Hz), 4.24−4.21 (2H, m, C*H*Ph and C*H*HOH), 4.11 (1H, ddd, J = 13.1, 9.6, 6.4 Hz, CH*H*OH), 3.46 (2H, br s, indenyl), 1.58 (1H, t, J = 6.4 Hz, O*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.80 (C), 144.46 (C), 143.82 (C), 140.16 (C), 128.97 (CH), 128.91 (2 × CH) 128.64 (2 × CH), 127.23 (CH), 126.23 (CH), 125.02 (CH), 123.94 (CH), 119.99 (CH), 66.13 (CH_2, *C*H_2OH), 47.54 (CH), 38.25 (CH_2, indenyl) ppm. IR (thin film): 3554 (s), 3399 (bs), 3060 (s), 2880 (s), 1602 (s), 1582 (m), 1493 (s), 1452 (s), 1393 (s), 1180 (bm), 1052 (bs) cm^{-1}. LRMS (EI): *m*/*z* 236 (M^+, 35%), 218 ($(M - OH_2)^+$, 24), 205 ($(M - CH_2OH)^+$, 100), 189 (9), 128 (24), 91 (21). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.13; H, 6.71.

Alcohol **6**: $[\alpha]_D^{25} = -19.1$ ($c = 2$, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (1H, ddt, J = 7.8, 0.9, 0.9 Hz), 7.44−7.41 (2H, m), 7.40 (1H, dt, J = 7.5, 0.9 Hz), 7.38−7.26 (4H, m), 7.22 (1H, td, J = 7.5, 1.3 Hz), 6.33 (1H, ddd, J = 3.4, 2.1, 1.3 Hz), 5.03 (1H, ddd, J = 7.9, 5.3, 2.5 Hz, C*H*(OH)Ph), 3.36 (2H, br s, indenyl), 3.01−2.97 (2H, m, CH_2 indenyl), 2.15 (1H, d, J = 2.6 Hz, *OH*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.84 (C), 144.39 (C), 144.07 (C), 140.72 (C), 131.03 (CH), 128.43 (2 × CH), 127.58 (CH), 126.11 (CH), 125.79 (2 × CH), 124.83 (CH), 123.87 (CH), 119.03 (CH), 72.49 (CH, *C*H(OH)Ph), 38.31 (CH_2, *C*H_2 indenyl), 37.31 (CH_2, indenyl) ppm. IR (thin film): 3400 (bs, OH), 3062 (m), 3028 (m), 2895 (m), 1606 (m), 1493 (m), 1455 (s), 1395 (s), 1201 (s), 1040 (bs), 970 (s), 913 (s), 873 (m) cm^{-1}. LRMS (EI): *m*/*z* 236 (M^+, 5%),130 (M^+ − PhCHO, 100), 107 (PhCH=O$^+$H, 31), 79 (26), 77 (15).

Synthesis of Toluene-4-sulfonic Acid (2*R*)-2-(3*H*-Inden-1-yl)-2-phenylethyl Ester (7). To a solution of (2*R*)-2-(3*H*-inden-1-yl)-2-phenylethanol (**5**; 3.55 g, 15 mmol) and dry pyridine (2.4 mL, 30 mmol) in dichloromethane (20 mL) was added *p*-toluenesulfonyl chloride (3.35 g, 16.6 mmol) portionwise at 0 °C. The reaction mixture was then stirred at 0 °C for 3 h and at room temperature for 15 h before cooling to 0 °C and adding diethyl ether (50 mL) followed by hydrochloric acid (50 mL, 2 M). The organic layer was separated and then washed with 5% aqueous sodium bicarbonate (45 mL) and water (45 mL) and dried over anhydrous magnesium sulfate. Removal of solvent in vacuo gave crude tosylate as an off-white solid. Recrystallization from hot ethanol afforded the title compound **7** as a white crystalline solid (4.32 g, 74%). Mp: 90−91 °C (sealed tube, under argon) (racemate mp 95−96 °C). $[\alpha]_D^{18} = -66.0$ ($c = 0.56$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (2H, d, J = 8.3 Hz), 7.40 (1H, m), 7.25−7.08 (9H, m), 6.99 (1H, m), 6.31 (1H, br d, J = 1.4 Hz), 4.57 (1H, dd, J = 9.7, 7.0 Hz), 4.39 (1H, dd, J = 9.7, 7.0 Hz), 4.29 (1H, td, J = 7.0, 1.1 Hz), 3.37 (2H, br s), 2.40 (3H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8 (C), 144.2 (C), 142.0 (C), 144.0 (C), 138.3 (C), 132.9 (C), 129.9 (2 × CH), 129.7 (CH), 128.9 (2 × CH), 128.5 (2 × CH), 128.0 (2 × CH), 127.5 (CH), 126.2 (CH), 125.0 (CH), 123.9 (CH), 119.7 (CH), 72.1 (CH_2), 44.1 (CH), 38.2 (CH_2), 21.8 (CH_3) ppm. IR ($CHCl_3$ solution): 3066 (m), 3032 (bs), 2892 (w), 1770 (bw), 1730 (bw), 1599 (m), 1494 (m), 1455 (m), 1360 (s, S=O), 1189 (s, S=O), 1097 (s), 972 (s), 880 (m), 701 (m) cm^{-1}. LRMS (EI): *m*/*z* 390 (M^+, 3%), 218 ($(M - TsOH)^+$, 100), 203 (25), 155 (10), 91 (20). Anal. Calcd for $C_{24}H_{22}SO_3$: C, 73.82; H, 5.68; Found: C, 73.78; H, 5.57.

Synthesis of (1*S*)-[2-(3*H*-Inden-1-yl)-1-phenylethyl]-diphenylphosphine (9). To a solution of tosylate **7** (1.56 g, 4 mmol), in THF (50 mL) at −78 °C was added dropwise via syringe potassium diphenylphosphide (8.8 mL of a 0.5 M solution in THF, 4.4 mmol). After addition was complete, the reaction mixture was stirred at −78 °C for 30 min before being warmed slowly to room temperature and stirred overnight, the color changing from bright red to orange. Degassed ethanol (5 mL) was added to quench the reaction; then approximately half the volume of solvent was removed via vacuum transfer. Toluene (50 mL) was added and the bright orange suspension filtered through silica under argon on an in-line sinter (eluent toluene) to give a pale green solution. The solvents were removed to give the title phosphine as a white air-sensitive solid (1.15 g, 70%). Mp: 98−99 °C. $[\alpha]_D^{18} = -114.9$ ($c = 2.1$, $CHCl_3$). ^{1}H NMR (300 MHz, C_6D_6): δ 7.89 (2H, t + fs, J = 7.5 Hz), 7.36 (2H, m), 7.05−7.30 (11H, m), 7.0 (4H, m), 5.85 (1H, br s), 4.026 (1H, apparent dt, J = 8.7, 6.2 Hz, C*H*Ph; in $CDCl_3$, where the adjacent CH_2 protons are not degenerate, it appears as a ddd, J_{HH} = 11, 3.3 Hz, J_{PH} = 6.3 Hz), 3.26 (2H, app t + fs, J_{HH} = 6.7 Hz, J_{PH} = 6.7 Hz, CH_2Ind), 2.995 (1H, d, J = 16 Hz, indenyl), 2.910 (1H, d, J = 16 Hz, indenyl) ppm. ^{13}C NMR (100 MHz, C_6D_6; numbering as for ligand moiety of **10** in Table 1): δ 145.65 (C, C7a), 144.50 (C, C3a), 142.20 (C, d, J_{CP} = 13.2 Hz, C1), 141.8 (C, d, J_{CP} = 8.3 Hz, C10), 138.0 (C, d, J_{CP} = 17.5 Hz, *i*-Ph), 137.65 (C, d, J_{CP} = 15.6 Hz, *i*-Ph), 134.6 (2 × CH, d, J_{CP} = 20.4 Hz, *o*-Ph), 133.75 (2 × CH, d, J_{CP} = 18.5 Hz, *o*-Ph), 130.13 (CH, *C2*), 129.56 (2 × CH, d, J_{CP} = 7.6 Hz, *m*-Ph), 129.51 (CH, *p*-Ph), 128.86 (2 × CH, d, J_{CP} = 7.3 Hz. *m*-Ph), 128.49 (CH, *p*-Ph), 128.38 (2 × CH, C12), 128.12 (2 × CH, d, J_{CP} = 6.3 Hz, C11), 126.38 (CH, d, J_{CP} = 2 Hz, C13), 126.26 (CH, C4/5/6/7), 124.80 (CH, C4/5/6/7), 123.93 (CH, C4/5/6/7), 119.20 (CH, C4/5/6/7), 44.77 (CH, d, J_{CP} = 14.4 Hz, C9), 37.84 (CH_2, C3), 32.34 (CH_2, d, J_{CP} = 24.7 Hz, C8) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ 1.07 (s) ppm. IR (CH_2Cl_2 solution): 3040 (bs), 2900 (bm), 1600 (bm), 1492 (s), 1453 (s), 1436 (s), 1280 (s), 1117 (m), 1019 (m), 895 (s), 775 (s), 603 (s) cm^{-1}. LRMS (EI): *m*/*z* 404 (M^+, 100%), 275 (Ph_2P^+=CHPh, 70), 219 ($(M - PPh_2)^+$, 53), 202 (87), 183 (35), 128 (70), 115 (50), 91 (84), 77 (61). Anal. Calcd (determined for BH_3 adduct; prepared as described for **19** below) for $C_{29}H_{28}BP$: C, 83.27; H, 6.75. Found: C, 83.19; H, 6.76.

Synthesis of *rac*-(*R*,*R*)-Spiro[(2-phenylcyclopropane)-1,1′-indene] (8). A solution of the racemic tosylate ***rac*-7** (0.78 g, 2 mmol) in THF (25 mL) was cooled to −78 °C and *n*-BuLi (0.96 mL of a 2.5 M solution in hexanes, 2.4 mmol, 1.2 equiv) added dropwise. After it was stirred at −78 °C for 15 min and room temperature for 2 h, the reaction mixture was quenched with water (20 mL) and the product extracted into diethyl ether (30 mL). The ether layer was washed with brine (20 mL) and then dried over $MgSO_4$. Concentration in vacuo, followed by recrystallization from hot ethanol, provided the spirocycle **8** (0.30 g, 69%) as off-white crystals, mp 79−81 °C. The crystals were suitable for X-ray crystallography, which confirmed the relative stereochemistry of **8**.[21] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (1H, d, J = 7.2 Hz), 7.02−7.29 (8H, m), 6.73 (1H, d, J = 5.7 Hz), 5.92 (1H, d, J = 5.5 Hz), 3.15 (1H, dd, J = 8.7, 7.2 Hz), 2.26 (1H, dd, J = 7.2, 5.0 Hz), 1.94 (1H, dd, J = 8.7, 5.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9 (C), 143.4 (C), 139.3 (C), 137.6 (CH), 129.9 (CH), 128.5 (2 × CH), 128.4 (2 × CH), 126.9 (CH), 126.0 (CH), 124.6 (CH), 121.6 (CH), 117.7 (CH), 41.1 (C), 33.3 (CH), 19.5 (CH_2) ppm. IR (thin film): 3044 (w), 1601 (m), 1497 (m), 1453 (s), 1200 (m), 1076 (m), 1048 (m), 1018 (m), 983 (s), 905 (m), 882 (m), 756 (s), 728 (s) cm^{-1}.

LRMS (AP^+): *m*/*z* 218 (M^+). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.44; H, 6.48.

Synthesis of *rac*-[2-(3*H*-Inden-1-yl)-1-phenylethyl]diphenylphosphine (9) from Spirocycle 8. To a solution of spirocycle **8** (0.218 g, 1 mmol) in THF (13 mL) at −78 °C was added dropwise potassium diphenylphosphide (2.2 mL of a 0.5 M solution in THF, 1.1 mmol). The reaction mixture was stirred at −78 °C for 30 min and room temperature for 2 h and then quenched with degassed ethanol (1 mL). The solution was concentrated to approximately half-volume, diluted with toluene (30 mL), and filtered through a bed of silica gel, under argon. Removal of solvent gave *rac*-**9** as a white solid (0.286 g, 71%), >90% pure by ^{1}H NMR.

Synthesis of (η^5:η^1-indenyl-$CH_2CH(Ph)PPh_2$)Rh^ICO (10). To (1*S*)-[2-(3*H*-inden-1-yl)-1-phenylethyl]diphenylphosphine (**9**; 0.808 g, 2 mmol) in THF (20 mL) under argon at −78 °C was added *n*-BuLi (0.8 mL, 2.5 M in hexanes, 2 mmol) dropwise to give a deep red solution. The solution was stirred at −78 °C for 30 min, warmed to room temperature, and stirred for a further 2 h. Meanwhile a golden yellow solution of [Rh^I(μ-Cl)-$(CO)_2]_2$ (0.389 g, 1 mmol), in THF (20 mL), was prepared under argon and cooled to −78 °C. The red anion solution was cooled to −78 °C and added via cannula dropwise over ca. 20 min to the THF solution of [Rh^I(μ-Cl)$(CO)_2]_2$ at −78 °C, immediately forming a dark orange-brown solution. The reaction mixture was stirred at −78 °C for 40 min before being warmed to room temperature and stirred overnight (ca. 16 h). The solvents were removed in vacuo to give a brown solid, which was purified by column chromatography (neutral grade III alumina, 20% petroleum ether/toluene) to afford the title complex as a yellow powder and a 3:1 mixture of diastereoisomers (0.764 g, 71%) (complexation of the racemic ligand gave a 5:2 mixture of diastereoisomers). There was no change in diastereoisomer ratios from the crude material on chromatography. Recrystallization from diethyl ether/pentane at −20 °C gave the diastereoisomerically pure complex **10** (0.324 g, 30%). Mp: 197−198 °C (racemate mp 195−197 °C). $[\alpha]_D^{18} = -105$ (*c* = 0.42, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6; numbering as in Table 1): δ 7.66 (2H, m, *o*-Ph[a]), 7.57 (2H, m, *o*-Ph[b]), 7.49 (1H, m, H7), 7.41 (1H, m, H4), 7.22 (2H, m, H5 + H6), 7.16 (1H, m, *p*-Ph[a]), 7.06 (3H, m, *m*-Ph[a] + H13), 6.99 (2H, t, J = 7.8 Hz, 2 H12), 6.96 (3H, m, *p*-Ph[b] + *m*-Ph[b]), 6.73 (2H, d + fs, 2 H11), 6.206 (1H, dd, J_{HP}* = 2.2 Hz, J_{HH} = 3.0 Hz, H2), 6.001 (1H, dd, J_{HP}* = 4.5 Hz, J_{HH} = 3.0 Hz, H3), 5.552 (1H, ddd, J_{HP} = 14 Hz, J_{HH} = 8.0, 6.0 Hz, H9), 2.813 (1H, dd, J_{HP} = 62.3 Hz, J_{HH} = 14.0, 5.8 Hz, H8[a]), 2.636 (1H, ddd, J_{HP} = 14 Hz, J_{HH} = 14.0, 8.0 Hz, H8[b]) ppm. The asterisk indicates that the couplings could be to Rh rather than P. ^{13}C NMR: see Table 1. ^{31}P NMR (120 MHz, C_6D_6): δ 86.2 (d, J_{PRh} = 214 Hz) ppm; minor isomer, in crude product, δ 84.1 (d, J_{PRh} = 214 Hz) ppm. IR ($CHCl_3$ solution): 3060 (bm), 2904 (w), 2337 (w), 1946 (s, CO), 1600 (m), 1479 (m), 1436 (s), 1320 (m), 1095 (s), 1010 (w), 864 (w), 698 (s), 540 (s), 504 (s) cm^{-1}. UV/vis (*c* = 3 mg/125 mL, CH_2Cl_2): λ_{max} 328 (ϵ 6898), 288 (ϵ 13 795), 204 (ϵ 24 920) nm. LRMS (EI): *m*/*z* 534 (M^+, 30%), 506 ($(M - CO)^+$, 100), 320 (50), 298 (14), 253 (7), 210 (12). Anal. Calcd for $C_{30}H_{24}RhPO$: C, 67.43; H, 4.53. Found: C, 67.40; H, 4.63.

Synthesis of (*S*)-1-Cyclohexyl-2-(3*H*-inden-1-yl)ethanol (14). A solution of indene (5.6 mL, 48 mmol) in THF (70 mL) was cooled to −78 °C, and *n*-BuLi (19.2 mL of a 2.5 M solution in hexanes, 48 mmol) was added dropwise. The resulting yellow suspension was stirred for 20 min at −78 °C, before being warmed to room temperature and stirred for 2 h. The anion solution was then cooled to −5 °C, and (*R*)-cyclohexyloxirane (5.05 g, 40 mmol) in THF (20 mL) was added dropwise and the mixture stirred at room temperature for 16 h. Saturated ammonium chloride solution (100 mL) was added and the product extracted into diethyl ether (3 × 100 mL). The combined organic layers were then washed with brine (100 mL) and dried over $MgSO_4$, and the solvents were removed in vacuo to yield a yellow solid. Column chromatography (SiO_2, 10% ethyl acetate/petrol) gave the title alcohol **14** as a white crystalline solid (6.93 g, 71.5%). Recrystallization from ethanol gave fine needles (mp 69−71 °C) of >99% ee by HPLC (250 × 5 mm Chiracel OD-H column, eluting with 0.7% isopropyl alcohol in hexane, 1 mL/min, R_t 17.5 min *R* enantiomer, R_t 21.0 min *S* enantiomer). The racemate had mp 60−62 °C. $[\alpha]_D^{26} = -34.9$ (*c* = 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (1H, d + fs, J = 7.3 Hz), 7.38 (1H, d + fs, J = 7.2 Hz), 7.31 (1H, td, J = 7.3, 1.1 Hz), 7.25 (1H, td, J = 7.2, 1.5 Hz), 6.38 (1H, br s), 3.73 (1H, ddd, J = 9.7, 5.6, 3.1 Hz, C*H*CyOH), 3.40 (2H, br s, indenyl), 2.88 (1H, dtd, J = 14.4, 3.3, 1.8 Hz, CH_2ind), 2.61 (1H, ddd, J = 14.4, 9.8, 1.1 Hz, CH_2ind), 1.10−1.90 (12H, m) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.2 (C), 144.7 (C), 141.8 (C), 130.7 (CH), 126.3 (CH), 125.0 (CH), 124.1 (CH), 119.3 (CH), 73.9 (CH), 43.6 (CH), 38.1 (CH_2), 33.2 (CH_2), 29.4 (CH_2), 28.3 (CH_2), 26.8 (CH_2), 26.5 (CH_2), 26.4 (CH_2) ppm. IR (Nujol mull): 3368 (bs), 2720 (m), 1580 (w), 1104 (m), 1026 (m), 991 (m), 966 (m), 914 (m), 891 (m) cm^{-1}. LRMS (AP^+): *m*/*z* 225 ($(M - OH)^+$, 19%), 224 ($(M - H_2O)^+$, 13), 131 ($(M - CyCH_2OH)^+$, 100). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.54; H, 9.21.

Synthesis of (*S*)-Methanesulfonic Acid 1-Cyclohexyl-2-(3*H*-inden-1-yl)ethyl Ester (15). To a stirred solution of alcohol **14** (5.94 g, 24.5 mmol) and triethylamine (8.5 mL, 6.2 g, 61.2 mmol) in dichloromethane (130 mL) at −30 °C was added dropwise methanesulfonyl chloride (2.5 mL, 3.7 g, 31.9 mmol). After it was stirred at −20 °C for 2 h, the solution was filtered and the organic phase washed with water (90 mL) and brine (90 mL) and then dried over $MgSO_4$ and concentrated in vacuo, yielding the crude product as a brown solid (6.63 g, ~77%), which was used immediately in the formation of the spirocycle **16**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (1H, d, J = 7.2 Hz), 7.43 (1H, d, J = 7.5 Hz), 7.34 (1H, t, J = 7.2 Hz), 7.24 (1H, t, J = 7.5 Hz), 6.39 (1H, br s), 5.85 (1H, ddd, J = 6.7, 6.7, 4.2 Hz), 3.37 (2H, br s), 2.99 (2H, d, J = 6.7 Hz), 2.62 (3H, s), 1.60−1.95 (7H, m), 1.20−1.40 (4H, m) ppm.

Synthesis of Methanesulfonic Acid (*R*)-1-Cyclohexyl-2-((methanesulfonyl)oxy)ethyl Ester (17). A stirred solution of (1*R*)-1-cyclohexyl-1,2-ethanediol (**12**; 6.49 g, 45 mmol) in dichloromethane (340 mL) was cooled to −30 °C, under argon. Triethylamine (22 mL, 158 mmol) was then added, followed by dropwise addition of methanesulfonyl chloride (8.7 mL, 113 mmol), causing the precipitation of a white solid. A further portion of dichloromethane (245 mL) was added to enable efficient stirring. The reaction mixture was stirred at −30 to −20 °C for 2 h and then filtered cold (−20 °C) and the residue washed with cold dichloromethane (120 mL, −20 °C). Water (300 mL) was then added to the collected filtrate, and the aqueous layer was separated and extracted with dichloromethane (3 × 180 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to yield the crude dimesylate as an off-white solid (14.82 g, ~109%). Recrystallization from dichloromethane/hexane at 5 °C gave three crops of the title compound as white crystals (13.1 g, 97%). All three crops retained the 97% ee of the diol starting material, as judged from their independent conversion into spirocyclopropane **16** of 97% ee. Mp: 114−116 °C. $[\alpha]_D^{25} = -17.2$ (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (1H, ddd, J = 6.6, 6.6, 2.6 Hz), 4.47 (1H, dd, J = 11.4, 2.6 Hz), 4.36 (1H, dd, J = 11.7, 6.6 Hz), 3.12 (3H, s), 3.10 (3H, s), 1.67−1.91 (6H, m), 1.03−1.37 (5H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.8 (CH), 67.3 (CH_2), 37.9 (CH_3), 37.8 (CH_3), 36.7 (CH), 27.5 (CH_2), 27.2 (CH_2), 24.8 (CH_2), 24.6 (CH_2), 24.5 (CH_2) ppm. IR (thin film): 3029 (w), 2958 (m), 2929 (m), 2857 (w), 1452 (w), 1355 (s), 1344 (s), 1332 (s), 1175 (s), 1034 (m), 979 (s), 904 (s), 844 (s), 792 (s) cm^{-1}. LRMS (AP^+): *m*/*z* 300.3 $(M)^+$. Anal. Calcd for $C_{10}H_{20}O_6S_2$: C, 39.99; H, 6.71. Found: C, 39.99; H, 6.74.

Synthesis of Spiro[(2-cyclohexylcyclopropane)-1,1′-indene] (16). From Mesylate 15. To a solution of the crude mesylate **15** (6.63 g, ~21 mmol) in THF (130 mL) at −78 °C under argon was added *n*-BuLi (11.9 mL, 2.5 M solution in

hexanes, 29.7 mmol). The reaction mixture was stirred at −78 °C for 15 min and then at room temperature for 2 h before quenching with water (40 mL). Diethyl ether (45 mL) was added, and the organic layer was separated, washed with brine (40 mL), and then dried over $MgSO_4$. Concentration in vacuo, followed by chromatography (SiO_2, petrol), provided the title product as a clear oil (3.45 g, 63% from **14**) and a 1:1 mixture of diastereoisomers.

From Bis-mesylate 17. A solution of indene (5.3 mL, 45 mmol) in THF (50 mL) was cooled to −78 °C and *n*-BuLi (18 mL of a 2.5 M solution in hexanes, 45 mmol) added dropwise, in the dark. The resulting yellow suspension was stirred at −78 °C for 15 min and then warmed to room temperature and stirred for 1.5 h. The anion mixture was cooled to 0 °C and diluted with THF (90 mL) and dimesylate **17** (5.6 g, 18.8 mmol) added portionwise over 2 min. The mixture was stirred at 0 °C for 15 min and then warmed to room temperature overnight (ca. 17 h). The reaction mixture was quenched with water (150 mL) and extracted with diethyl ether (4 × 75 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (150 mL) and then dried over $MgSO_4$ and concentrated in vacuo. Chromatography (SiO_2, petrol) gave the desired product contaminated with a small amount of indene, which was removed by evaporation under vacuum (0.3 mmHg) for 24 h at room temperature, to yield the clean spirocycle **16** as a white solid (3.56 g, 84%) and a 9:2 mixture of diastereoisomers. Chiral HPLC (250 × 5 mm Chiracel OD-H column, eluting with 1% isopropyl alcohol in hexane, 1 mL/min, R_t = 4.7 min (minor isomer, + enantiomer), R_t = 4.9 min (major isomer, + enantiomer), R_t = 5.4 min (major isomer, − enantiomer), R_t = 7.3 min (minor isomer, − enantiomer)) showed the product has retained chirality (97% ee) from the diol **12**. Recrystallization from hot ethanol afforded the enantiopure major isomer as clear crystals, mp 79−80 °C. $[\alpha]_D^{25}$ = +216.0 (c = 0.5, $CHCl_3$) (major isomer). ^{1}H NMR (400 MHz, major diastereoisomer, $CDCl_3$): δ 7.44 (1H, dt, J = 7.4, 0.9 Hz), 7.25 (1H, td, J = 7.4, 1.1 Hz), 7.18 (1H, td, J = 7.4, 0.9 Hz), 6.97 (1H, dt, J = 7.4, 0.9 Hz), 6.97 (1H, d, J = 5.7 Hz), 6.41 (1H, d, J = 5.7 Hz), 2.00 (1H, m), 2.00−1.50 (5H, m), 1.72 (1H, dd, J = 8.5, 4.3 Hz), 1.61 (1H, dd, J = 7.2, 4.3 Hz), 1.37−1.12 (4H, m), 1.24 (1H, dd, J = 11.1, 8.6 Hz), 0.94 (1H, m) ppm. ^{13}C NMR (100 MHz, major diastereoisomer, $CDCl_3$): δ 148.94 (C), 143.09 (C), 138.01 (CH), 129.38 (CH), 125.40 (CH), 124.34 (CH), 121.42 (CH), 117.56 (CH), 42.15 (CH), 38.08 (C), 37.04 (CH_2), 33.56 (CH_2), 33.28 (CH_2), 26.65 (CH_2), 26.56 (CH_2), 26.31 (CH_2), 21.60 (CH_2) ppm. IR (thin film): 3029 (w), 2958 (m), 2929 (m), 2857 (w), 1452 (m), 1355 (s), 1344 (s), 1332 (s), 1175 (s), 1034 (m), 979 (s), 904 (bs), 844 (s), 793 (s), 762 (m), 739 (m) cm^{-1}. LRMS (AP$^+$): m/z 225 ((M + H)$^+$, 42%), 224 (M$^+$, 100), 181 (9), 168 (11). Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 91.16; H, 9.02.

Synthesis of [(2*R*)-2-Cyclohexyl-2-(3*H*-inden-1-yl)ethyl]diphenylphosphine (18). To a solution of spiro-[(2-cyclohexylcyclopropane)-1,1′-indene] (**16**; 2.02 g, 9.0 mmol) and 18-crown-6 (48 mg, 2 mol %) in THF (45 mL) at 0 °C was added dropwise a deep red solution of potassium diphenylphosphide (21.6 mL of a 0.5 M solution in THF, 10.8 mmol). The reaction mixture was stirred at room temperature for 48 h before quenching with degassed ethanol (10 mL). Approximately half the THF was removed by vacuum transfer, the residue diluted with toluene (30 mL), and the mixture filtered through a 3 cm bed of silica under argon, washing through with more toluene (60 mL). Removal of solvent and chromatography of the crude product (SiO_2, 0−3% ethyl acetate in hexane) under argon gave the title compound as a white, cloudy, air-sensitive oil (3.26 g, 88%), with no oxidized product present in the mass spectrum. $[\alpha]_D^{26}$ +23.0 (c = 1.0, $CHCl_3$). Numbering in ^{1}H and ^{13}C NMR as for ligand moiety of **20** in Table 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12−7.41 (14H, m), 6.12 (1H, t, J = 1.8 Hz, H2), 3.24 (2H, d, J = 1.8 Hz, H3), 2.64 (1H, dddd, J_{HH} = 10.2, 6.2, 4.2 Hz, J_{HP} = 10.2 Hz, H8), 2.55 (1H, ddd, J_{HH} = 13.6, 4.2 Hz, J_{HP} = 3.0 Hz, H9), 2.40 (1H, ddd, J_{HH} = 13.6, 10.2 Hz, J_{HP} = 2.0 Hz, H9), 1.53−1.89 (6H, m, cyclohexyl ring), 0.85−1.23 (5H, m, cyclohexyl ring) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.46 (C, d, J_{CP} = 3.9 Hz, C1), 145.65 (C, C3a/7a), 144.94 (C, C3a/7a), 139.99 (C, d, J_{CP} = 13.5 Hz, *i*-Ph), 139.15 (C, d, J_{CP} = 15.0 Hz, *i*-P*h*), 133.49 (2 × CH, d, J_{CP} = 19.3 Hz, *o*-Ph), 132.69 (2 × CH, d, J_{CP} = 18.3 Hz, *o*-Ph), 129.89 (CH, d, J_{CP} = 1.5 Hz, C2), 128.84 (CH, *p*-Ph), 128.54 (2 × CH, d, J_{CP} = 6.8 Hz, *m*-Ph), 128.32 (2 × CH, d, J_{CP} = 6.3 Hz, *m*-Ph), 128.27 (CH, *p*-Ph), 125.91 (CH, C4/5/6/7), 124.52 (CH, C4/5/6/7), 123.98 (CH, C4/5/6/7), 119.96 (CH, C4/5/6/7), 42.47 (CH, d, J_{CP} = 8.2 Hz, CH of cyclohexane), 41.68 (CH, d, J_{CP} = 14.0 Hz, *C8*), 37.91 (CH_2, *C3*), 31.05 (2 × CH_2, d, J_{CP} = 6.3 Hz, $CHCH_2$ of cyclohexane), 30.76 (CH_2, d, J_{CP} = 12.1 Hz, C9), 26.78 (2 × CH_2, cyclohexane), 26.75 (CH_2, cyclohexane) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ −17.9 (s) ppm. IR (thin film): 3068 (w), 2923 (bs), 2850 (bm), 1585 (w), 1480 (w), 1448 (m), 1433 (m), 1393 (w), 1263 (w), 1095 (m), 1026 (m), 969 (m), 915 (w), 845 (w), 769 (s), 738 (s), 696 (s) cm^{-1}. LRMS (ES$^+$): m/z 411.4 (M + H)$^+$ (fully oxidized by air when in solution: m/z 427.3, (M + O + H)$^+$). Anal.: determined for BH_3 derivative **19** (see below).

Synthesis of 2-Cyclohexyl-2-(3*H*-inden-1-yl)ethyl]diphenylphosphine−Borane Complex (19). i. From Addition of Borane to Ligand 18. A solution of cyclohexyl-substituted ligand **18** (180 mg, 0.44 mmol) was prepared in THF (10 mL) under argon and cooled to 0 °C. A solution of borane−dimethyl sulfide complex (0.05 mL, 0.53 mmol) in THF (1 mL) was then added dropwise. The clear reaction mixture was stirred at 0 °C for 30 min before quenching by addition of ice−water (10 mL) at 0 °C and extraction of the product into ethyl acetate (4 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, then concentrated in vacuo. Recrystallization of the crude product from hexane at −30 °C gave the title compound as a white air-stable solid (125 mg, 68%).

ii. By Ring Opening of Spirocycle 16 with [Ph_2-PBH_3]$^-$$Li^+$. A solution of lithium diphenylphosphide−borane complex[35] (4 mL of a 0.25 M solution in THF, 1.0 mmol) and HMPA (0.14 mL, 0.83 mmol) was prepared and cooled to 0 °C, under argon. A solution of spiro[(2-cyclohexylcyclopropane)-1,1′-indene] (**16;** 186 mg, 0.83 mmol) in THF (1 mL) was then added dropwise. The reaction mixture was stirred for 15 min at 0 °C, then warmed to room temperature, and stirred for 24 h. The reaction was quenched with water (2 mL), and the product was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and then concentrated in vacuo. The product was purified by column chromatography (SiO_2, 10% ethyl acetate in petrol) and isolated as a white solid (212 mg, 61%). Mp: 124−126 °C (enantiopure). $[\alpha]_D^{25}$ = −14.0 (c = 0.5, $CHCl_3$). Numbering of ^{1}H and ^{13}C NMR as in the ligand moiety of **20** in Table 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.607 (2H, t + fs, J = 8.3 Hz), 7.35−7.41 (6H, m), 7.325 (1H, d, J = 7.4 Hz), 7.240 (2H, br t, J = 8.8 Hz), 7.19 (1H, tq, J = 7.4, 1.4 Hz), 7.126 (1H, td, J = 7.4, 1.0 Hz), 7.050 (2H, tq, J = 7.7, 2 Hz), 5.942 (1H, t, J = 2 Hz, H2), 3.187 (1H, dddd, J = 12.7, 10.3, 7.5, 2.6 Hz, H8), 2.7−2.9 (3H, m, 2 H3 + H9), 2.575 (1H, ddd, J = 14.2, 9.4, 2.8 Hz, H9), 1.931 (1H, br d, J = 12.5 Hz), 1.5−1.8 (5H, m), 0.85−1.25 (8H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.83 (C, s, C1/7a/3a), 144.71 (C, s, C1/7a/3a), 144.62 (C, s, C1/7a/3a), 132.74 (2 × CH, d, J_{CP} = 9.2 Hz, *o*-Ph), 132.00 (2 × CH, d, J_{CP} = 8.7 Hz, *o*-Ph), 131.67 (CH, br d, J_{CP}* = 11.4 Hz, C2), 131.06 (CH, br d, J_{CP}* = 21.8 Hz, *i*-Ph), 130.96 (CH, d, J_{CP} = 2.2 Hz, *p*-Ph), 130.72 (CH, d, J_{CP} = 2.4 Hz, *p*-Ph), 128.85 (2 × CH, d, J_{CP} = 9.7 Hz, *m*-Ph), 128.83 (C, d, J_{CP}* = 33.8 Hz, *i*-Ph), 127.96 (2 × CH, d, J_{CP} = 9.9 Hz, *m*-Ph), 125.82 (CH, s, C7/4/6/5), 124.49 (CH, s, C7/4/6/5), 123.85 (CH, s, C7/4/6/5), 120.23 (CH, s, C7/4/6/5), 42.39 (CH, br d, J_{CP}* = 9.2 Hz, C10), 39.87 (CH, br s,* C8), 37.64 (CH_2, s, C3), 31.27 (CH_2, s, C11), 30.74 (CH, s, C11′), 27.35 (CH_2, br d,

J_{CP}* = 36.0 Hz, C9), 26.66 (CH_2, s, C12/12′/13), 26.59 (CH_2, s, C12/12′/13), 26.58 (CH_2, s, C12/12′/13) ppm. The asterisks indicate that these signals and coupling constants were difficult to distinguish, owing to borane-broadening of the ^{13}C resonances. LRMS (AP^+): *m/z* 464.5 ($(M - H + CH_3CN)^+$, 72%), 423.3 ($(M - H)^+$, 100), 411.2 ($(M - BH_3 + H)^+$, 67). IR (thin film): 2933 (bm), 2914 (bm), 2848 (m), 1458 (m), 1436 (s), 1107 (m), 1064 (s), 965 (m), 870 (m), 791 (m), 767 (s), 747 (m), 727 (s) cm^{-1}. Anal. Calcd for $C_{29}H_{34}BP$: C, 82.08; H, 8.08; P, 7.30. Found: C, 82.22; H, 8.18; P, 7.37.

Deprotection of the Borane Complex 19. The borane-protected phosphine ligand (50 mg, 0.12 mmol) was treated with neat diethylamine (1 mL), under argon and warmed to 50 °C. The reaction mixture was stirred with monitoring by TLC (10% ethyl acetate in petrol) for 3 h. After this time TLC showed the deprotected phosphine ligand present at R_f 0.6, along with remaining borane-protected phosphine at R_f 0.4. The reaction mixture was cooled and then evacuated to dryness, to remove remaining diethylamine and the diethylamine−borane complex. Fresh diethylamine (1 mL) was then added to the mixture of starting material and product, and the reaction mixture was heated again to 50 °C overnight. After this time, TLC showed only the free phosphine present. The reaction mixture was then cooled and evacuated to dryness, leaving the ligand **18** as an air-sensitive oil (48 mg, 99%). ^1H NMR was identical with that of **18** prepared above.

Synthesis of (η^5:η^1-indenyl-CH(Cy)CH_2PPh_2)Rh^ICO (20). To a solution of chiral ligand **18** (0.41 g, 1 mmol) in THF (20 mL) under argon at −78 °C was added slowly *n*-BuLi (0.4 mL of a 2.5 M solution in hexanes, 1.0 mmol), and the reaction mixture was stirred at −78 °C for 30 min and then warmed to room temperature and stirred for a further 2 h. The dark red ligand anion solution was then cooled to −78 °C and added via cannula dropwise over ca. 20 min to a solution of $[Rh^I(\mu\text{-}Cl)(CO)_2]_2$ (194 mg, 0.5 mmol) in THF (20 mL) at −78 °C, immediately forming a dark brown solution. This solution was stirred at −78 °C for 2 h before being warmed slowly to room temperature, overnight (16 h). The solvents were then removed in vacuo, to give a brown foamy solid. ^1H NMR spectroscopy showed the desired complex formed as a 78:22 mixture of **20** and **21** (using the racemic ligand, the ratio was typically 72:28). The crude material was purified by column chromatography (neutral alumina, 30−50% toluene in petrol) to afford the product as an orange powder (367 mg, 68%). There was no change in isomer ratios from the crude product on chromatography. Recrystallization from diethyl ether/hexane at −30 °C afforded the major diastereoisomer **20** as clear red crystals (195 mg, 36%). Mp (chiral): 168 °C dec (sealed tube). $[\alpha]_D^{21} = -75.6$ ($c = 1$, $CHCl_3$). Mp (racemic): 170 °C dec (sealed tube). ^1H NMR (400 MHz, C_6D_6; numbering as in Table 1): δ 7.75−7.68 (2H, m, *o*-Ph), 7.59 (2H, ddd, $J_{HP} = 11.7$ Hz, $J_{HH} = 7.8$, 1.7 Hz, *o*-Ph), 7.38 (1H, d + fs, $J_{HH} = 8.0$ Hz, H4), 7.21−7.17 (4H, m, *m*-Ph + *p*-Ph + H6), 7.12−7.08 (3H, m, *m*-Ph + *p*-Ph), 7.07 (1H, ddd, $J_{HH} = 8.0$, 7.0, 1.0 Hz, H5), 6.98 (1H, d + fs, $J_{HH} = 8.0$ Hz, H7), 6.20 (1H, dd, $J_{HH} = 2.8$ Hz, J_{HP}* = 2.7 Hz, H3), 6.14 (1H, dd, $J_{HH} = 2.8$ Hz, J_{HP}* = 2.5 Hz, H2), 3.30 (1H, dddd, $J_{HP} = 13.3$ Hz, $J_{HH} = 13.3$, 4.6 Hz, $J_{HRh} = 2.5$ Hz, H9), 2.93 (1H, ddd, $J_{HH} = 13.6$, 13.3 Hz, $J_{HP} = 7.0$ Hz, H9), 2.63 (1H, dddd, $J_{HH} = 13.6$, 4.6, 4.6 Hz, $J_{HP} = 9.0$ Hz, H8), 1.80−0.72 (11H, m, cyclohexyl ring) ppm. Asterisks denote where the coupling could be to Rh rather than P. ^{13}C NMR (100 MHz, C_6D_6): see Table 1. IR (CH_2Cl_2 solution): 2929 (m), 2853 (m), 1939 (s, CO), 1479 (w), 1436 (w), 1095 (w) cm^{-1}. LRMS (AP^+) *m/z* 554 ($(M + CH_3CN + H - CO)^+$, 100%), 553 ($(M + CH_3CN - CO)^+$, 46), 541 ($(M + H)^+$, 33), 513 ($(M + H - CO)^+$, 10), 512 ($(M - CO)^+$, 4). Anal. Calcd for $C_{30}H_{30}OPRh$: C, 66.67; H, 5.60; P, 5.73. Found: C, 66.71; H, 5.67; P, 5.67.

X-ray Crystallography of Complexes 10 and 20. A summary of crystal data, intensity collection details, and refinement parameters is reported in Table 2. A single crystal of **10** or **20** was mounted on a glass fiber, and data collections were performed at 150 K using an Enraf-Nonius Kappa CCD area detector (λ(Mo Kα) = 0.710 73 Å).[37] In each case the data were corrected for absorption effects using SORTAV[38] and the structures solved by direct methods using SHELXS97.[39] Hydrogen atoms were included in calculated positions, and all atoms were refined anisotropically using full-matrix least-squares refinement on F^2 (SHELXL97[40]) to give R1 = 0.0444 and wR2 = 0.0995 for **10** and R1 = 0.0432 and wR2 = 0.0764 for **20**. For **10** the absolute stereochemistry was confirmed by determination of the Flack absolute structure parameter *x* as −0.0349 (esd 0.0271).

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Supporting Information Available: Listings of all fractional atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for **10** and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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